PB82-119090

DETERMINATION OF VOLATILE ORGANICS IN INDUSTRIAL AND MUNICIPAL WASTEWATERS

J. L. Wilson

Carborundum Company
Niagara Falls, NY

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DETERMINATION OF VOLATILE ORGANICS IN INDUSTRIAL AND MUNICIPAL WASTEWATERS

by

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Contract No. 68-03-2635

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This report describes the systematic evaluation of a series of parameters leading to the development of a test procedure for 36 volatile priority pollutants in wastewaters. A study of the effect of pH, temperature, and residual chlorine on the aqueous stability of the compounds leads to recommended preservation techniques. Solvent extraction and purge and trap techniques are examined, with special emphasis on trap material, GC packings and detectors. The resulting test procedures were applied to selected wastewaters to develop accuracy and precision data. The study included the following compounds: benzene, chlorobenzene, toluene, ethylbenzene, carbon tetrachloride, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1-dichloroethane, 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane, chloroethane, chloroform, 1,1-dichloroethane, 1,2-trans-dichloroethane, 1,2-dichloropropane, 1,3-cis-dichloropropene, 1,3-trans-dichloropropene, methylene chloride, methyl chloride, methyl bromide, bromoform, dichlorobromomethane, trichlorofluoromethane, chlorodibromomethane, tetrachloroethene, trichloroethene, vinyl chloride, 2-chloroethylvinyl ether, 2,3-dichloropropene, dibromomethane, 1,2-dibromoethane, 1-chlorocyclohexene, p-dichlorobenzene, acrolein, acrylonitrile, dichlorodifluoromethane.

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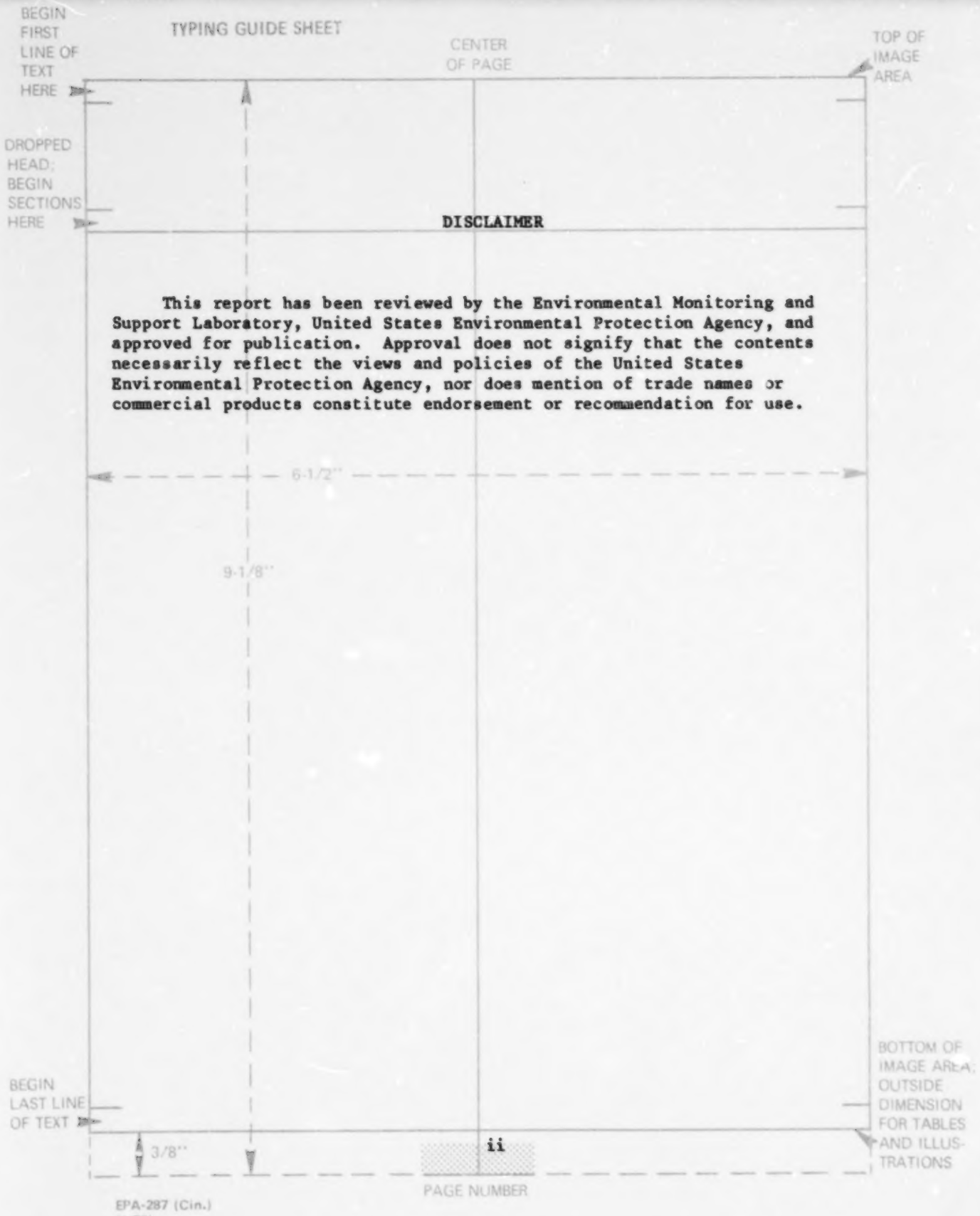
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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati conducts research to:

- Develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria, and other microbiological organisms in water. Conduct studies to determine the responses of aquatic organisms to water quality.
- Conduct an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

Under provisions of the Clean Water Act, the Environmental Protection Agency is required to promulgate guidelines establishing test procedures for the analysis of pollutants. The Clean Water Act Amendments of 1977 emphasize the control of toxic pollutants and declare the 65 "priority" pollutants and classes of pollutants to be toxic under Section 307(a) of the Act. This report is one of a series that investigates the analytical behavior of selected priority pollutants and suggests a suitable test procedure for their measurement.

Robert L. Booth

Robert L. Booth, Acting Director
Environmental Monitoring and Support Laboratory - Cincinnati

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ABSTRACT

This program was undertaken in an effort to develop analytical methodologies for the determination of volatile organics in industrial and municipal wastewaters. The efforts were directed exclusively toward analytical techniques employing gas chromatography with flame ionization and halogen-specific detectors.

A number of gas chromatographic column packings were evaluated in an effort to find a set of optimum operating conditions. Direct aqueous injection, solvent extraction, and purge and trap techniques were evaluated as means of sample introduction. The most satisfactory results were obtained using the Bellar-Lichtenberg purge and trap method with both FID and Coulson detectors.

Stability of the test compounds as solutions in methanol and n-butanol was evaluated after 30-, 60-, and 90-day periods. Preservation of aqueous samples containing residual chlorine for a one week period was studied; aliquots of reducing agents, added to the sample before storage, were found to aid in maintaining chemical stability.

The methods developed were tested on spiked industrial wastewater samples in order to evaluate their applicability to real world situations. The methods were found to be satisfactory for relatively "clean" samples. For grossly contaminated samples, however, the methods suffer from interferences caused by lack of detector specificity.

This report was submitted in fulfillment of contract No. 68-03-2635 by California Analytical Laboratory working as a subcontractor to The Carborundum Company under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period May, 1978 to June, 1979.

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SECTION 1

INTRODUCTION

Several techniques are available for analysis of volatile organic compounds in wastewaters. For complex samples the currently accepted methodology for determination of volatile priority pollutants in industrial and municipal wastewaters employs the Bellar-Lichtenberg purge and trap technique coupled with gas chromatography/mass spectrometry. There is increasing need for simpler and less expensive analytical methodologies using more common laboratory instrumentation.

The purpose of the present study was to develop and evaluate various techniques for analysis of volatile organics by gas chromatography with various detectors (exclusive of the mass spectrometer). Thirty-six compounds were studied. While the focus of this study was to develop analytical methods specifically for these compounds, the methods developed could apply to analysis of other compounds as well. A list of the compounds studied is found in Table 1.

The study was conducted in two major phases. In Phase I, analytical methods were developed. Several gas chromatographic column packing materials were evaluated with respect to their ability to separate as many of the compounds as possible. Detection was accomplished by means of flame ionization, electron capture, and Coulson electrolytic conductivity detectors. Direct aqueous injection, liquid/liquid extraction, and purge and trap techniques were studied as methods of sample introduction.

The stability of the test compounds in solutions of methanol and butanol were evaluated in 30-, 60-, and 90-day stability tests. The effects of storage conditions upon the chemical stability of aqueous samples containing trace levels of test compounds and residual chlorine were studied. An effort was made to determine a set of optimum conditions for water sample storage.

In Phase II of the study, the methods developed in Phase I were applied to the analysis of industrial wastewaters. Samples from five industrial categories were analyzed by direct injection using FID and Coulson detectors, by liquid extraction using the electron capture detector, and by purge and trap using FID and Coulson detectors. The results of the various analyses were compared for each of the industrial samples.

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TABLE 1. COMPOUNDS UNDER INVESTIGATION

benzene	methyl choloride
chlorobenzene	methyl bromide
toluene	bromoform
ethylbenzene	dichlorobromomethane
carbon tetrachloride	trichlorofluoromethane
1,2-dichloroethane	chlorodibromomethane
1,1,1-trichloroethane	tetrachloroethylene
1,1-dichloroethane	trichloroethylene
1,1,2-trichloroethane	vinyl chloride
1,1,2,2-tetrachloroethane	2-chloroethylvinyl ether
chloroethane	2,3-dichloropropene[a]
chloroform	dibromomethane[a]
1,1-dichloroethylene	1,2-dibromoethane[a]
1,2-trans-dichloroethylene	1-chlorocyclohexene[a]
1,2-dichloropropane	p-dichlorobenzene
1,3-cis-dichloropropylene	acrolein
1,3-trans-dichloropropylene	acrylonitrile
methylene chloride	dichlorodifluoromethane

[a]Compounds not on the EPA list of priority pollutants

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SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

Methodologies for the analysis of volatile organic compounds in industrial and municipal wastewaters have been developed and evaluated, using gas chromatography with the flame ionization, electron capture, and Coulson detectors. Several improvements in existing analytical methods have been realized. Some of the current techniques need further development.

Although no single GC column was found that gives complete chromatographic separation of all the test compounds, several GC packing materials were identified that provide good chromatographic separation of all but a few of the test compounds. These GC packings are described in detail in the main portion of this report.

All of the test compounds were detected by one or more of the analytical approaches studied at levels of 1ppb or less. The nonhalogenated compounds are not detected by Coulson or electron capture. Many of the compounds are detectable at levels of 0.1 ppb or lower.

The stability of the test compounds as standards in organic and as "clean" samples in aqueous media was studied in detail. The addition of preservatives to reduce residual chlorine in aqueous samples was found to help maintain the integrity (chemical stability) of aqueous samples containing residual chlorine and trace quantities of the test compounds.

The major limitation of all the analytical approaches investigated in this study was the lack of specificity of detection. The FID was the only detector of those studied that was able to detect the nonhalogenated compounds. However, it was the least specific of the detectors studied. For relatively "clean" wastewaters, a combination of the analytical methods developed on this project have been found to usually be both specific and sensitive. However, for grossly polluted wastewaters, interferences became such a severe problem that qualitative identification was not feasible.

Further study is recommended to develop either sample clean-up procedures for use prior to analysis, or to find an analytical scheme more specific to the test compounds of interest before these or similar methods can become generally applicable for analysis of complex industrial or municipal wastewaters. Other areas recommended for further study are: further evaluation of the precision and accuracy of the methods developed herein, evaluation of alternative trap materials to be used in the purge and trap approach, further evaluation of the effects of antifoaming agents

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on the precision and accuracy of purge and trap methods, and development of alternative methods for the analysis of acrolein and acrylonitrile.
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SECTION 3

DEVELOPMENT OF ANALYTICAL METHODS

GENERAL

In the first phase of this program three approaches for analyzing wastewater for thirty-six volatile organic compounds were evaluated: the purge and trap technique of Bellar and Lichtenberg[1,2], the direct aqueous injection approach, and the solvent extraction approach. The first two approaches employed both the flame ionization detector (FID) and the Coulson electrolytic conductivity detector. The third approach utilized the electron capture detector (ECD). Except as specified later, all of the chromatographic column packing materials tested were compatible with any of the analytical approaches.

The stability of the test compounds in alcoholic solutions was evaluated in 30-, 60-, and 90-day intervals. Preservation of aqueous samples containing trace levels of the test compounds and residual chlorine was studied in an effort to find an optimum set of conditions for storage of real-world samples.

CHROMATOGRAPHY

No gas chromatographic column has yet been found which will separate all the test compounds in a single programmed run. Three packings were tried, specifically 3% SP-2510, Tenax GC, and Chromosorb 102 and found to be unsatisfactory for general use. These columns were rejected primarily because of inadequate separation of a number of compounds, or, in some cases, because of poor chromatography. For a specific subset of the purgeables, however, these column materials may be suitable in a given wastewater.

Three columns which did show adequate separation of most compounds, and good chromatography (sharp peaks, no tailing) were 1% SP-1000 on Carbopack B (60-80 mesh), 0.2% Carbowax 1500 on Carbopack C (60-80 mesh), and 20% SP-2100/0.1% Carbowax 1500 on Supelcoport (100-120 mesh). The retention times of each compound on these columns along with the column dimensions and temperature programs are given in Table 2. A summary of the incomplete compound separations on each column are given in Table 3. A close examination will show that those compounds which do not separate on the 1% SP-1000 column, for example, will separate on the 20% SP-2100, and vice versa. Thus, by comparing retention times on two columns, one can get sufficient separation of all compounds. For the columns and programs used,

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TABLE 2. RETENTION TIMES OF TEST COMPOUNDS

	Compound	Retention times (min.) Column 1	Column 2	Column 3
1	dichlorodifluoromethane	1.7	0.95	1.3
2	methyl chloride	0.7	0.54	1.8
3	vinyl chloride	--	1.0	1.6
4	methylbromide	1.4	0.8	2.2
5	chloroethane	2.5	1.3	2.5
6	trichlorofluoromethane	6.3	2.3	5.0
7	1,1-dichloroethylene	6.9	3.6	3.4
8	methylene chloride	4.1	4.5	3.6
9	1,2-trans-dichloroethylene	8.8	5.2	4.7
10	acrolein	4.7	4.2	2.5
11	1,1-dichloroethane	8.2	4.5	5.6
12	chloroform	9.3	6.7	5.9
13	1,1,1-trichloroethane	10.9	8.8	9.2
14	carbon tetrachloride	11.3	9.3	8.2
15	acrylonitrile	5.4	4.8	3.2
16	benzene	14.0	13.8	8.8
17	1,2-dichloroethane	10.0	7.5	8.2
18	trichloroethylene	13.6	12.7	9.9
19	dichlorobromomethane	11.8	10.5	10.2
20	2,3-dichloropropene	12.9	11.5	10.0
21	1,2-dichloropropane	12.9	11.6	10.3
22	dibromomethane	10.1	10.0	10.4
23	1,3-trans-dichloropropylene	13.1	12.1	10.8
24	2-chloroethylvinyl ether	15.0	14.0	10.7
25	toluene	19.1	23.3	11.7
26	1,3-cis-dichloropropene	14.2	13.5	11.0
27	1,1,2-trichloroethane	14.2	13.6	11.3
28	chlorodibromomethane	14.0	13.6	12.6
29	1-chlorocyclohexene	18.7	--	14.3
30	tetrachloroethylene	18.1	18.3	13.4
31	1,2-dibromoethane	14.9	14.4	12.7
32	chlorobenzene	20.0	20.4	13.0
33	ethylbenzene	21.8	26.7	13.7
34	1,1,2,2-tetrachlorethane	18.0	18.6	14.5
35	bromoform	16.2	16.3	14.1
36	p-dichlorobenzene	27.3	--	17.2

Column 1: 1.8 m x 2 mm glass with 1% SP1000 on Carbopack B, 60-80 mesh; Program-Inject at 50°C; hold 5 min., then up 10°c/min. to 225°C for 5 min.

Column 2: 1.8 m x 2 mm glass with 0.2% Carbowax 1500 on Carbopack C, 60-80 mesh; Program Inject at 40°C; hold 4 min., up 10°C/min to 175°C, hold 10 min.

Column 3: 4 m x 2 mm i.d. glass with 20% SP2100/0.1% Carbowax 1500 on 100-125 mesh Supelcoport; Program-Inject at 50°C; hold 4 min., up 10°C/min. to 170°C, hold four minutes.

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TABLE 3. COMPOUNDS WHICH ARE DIFFICULT TO SEPARATE

Column	Coupounds Having Same Retention Time	Retention Time (min)
	benzene 1,3-cis-dichloropropylene	
	1,1,2-trichloroethane chlorodibromomethane	14.0-14.2
1) 1% SP1000 on 60-80 mesh Carbopack	1,2-dichloroethane dibromomethane	10.0
	2,3-dichloropropene 1,2-dichloropropane 1,3-trans-dichloropropylene	12.9-13.1
	tetrachloroethylene 1,1,2,2-tetrachloroethane	18.1
	vinyl chloride methylbromide	0.8- 1.0
	methylene chloride	
2) 0.2% Carbowax 1500 on 60-80 mesh Carbopack C.	1,1-dichloroethane	4.5
	1,3-cis-dichloropropylene 1,1,2-trichloroethane chlorodibromomethane	13.5
	tetrachloroethylene 1,1,2,2-tetrachloroethane	18.3-18.6
	trichlorofluoromethane 1,2-trans-dichloroethylene	4.7- 5.0
	1,1-dichloroethylene acrylonitrile	3.2- 3.4
3) 20% SP 2100/0.1% Carbowax 1500 on 100-120 mesh Supelcoport	1,1-dichloroethene methylene chloride	3.4- 3.6
	acrolein chloroethane	2.5
	carbon tetrachloride 1,2-dichloroethane	8.1
	trichloroethylene dichlorobromomethane 2,3-dichloropropene	9.9-10.2
	2,3-dichloropropene dichlorobromomethane 1,2-dichloropropane	10.0-10.3
	dichlorobromomethane 1,2-dichloropropane dibromomethane	10.2-10.4
	1,3-cis-dichloropropylene 1,1,2-trichloroethane	11.0-11.3
	1-chlorocyclohexene 1,1,2,2-tetrachloroethane	14.3-14.5

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a difference in retention time of 0.3 min was sufficient to give almost baseline separation of the test compounds, and thus sufficient for quantitation. A separation of 0.2 min was adequate to show that two compounds were present. These criteria were especially applicable when using the FID or the electron capture detector. There is a slight loss of resolution when using the Coulson detector, but not enough to make the above criteria inoperative.

Additional work with a 4m x 2mm ID glass column of 10% SP-2250 showed that it gave good separation of most of the compounds which did not separate on Column 3 in Table 2. The comparable separations are shown in Table 4. The chromatographic conditions and temperature program are identical to those listed in Table 2.

TABLE 4. COMPARISON OF RETENTION TIMES FOR SELECTED COMPOUNDS

Compound	Retention Time (min.) Column 3	10% SP-2250
carbon tetrachloride	8.2	7.8
1,2-dichloroethane	8.2	8.9
trichloroethylene	9.9	9.4
dichlorobromomethane	10.2	10.4
2,3-dichloropropene	10.0	10.0
1,2-dichloropropane	10.3	9.9
dibromomethane	10.4	10.6
1,3-cis-dichloropropylene	11.0	11.9
1,1,2-trichloroethane	11.3	12.2

PURGE AND TRAP

The purge and trap technique of Bellar and Lichtenberg has been investigated in detail and evaluated with respect to its ability to detect ppb levels of the test compounds. Data has been obtained that demonstrates the ability of this method to detect 1 ppb of all the test compounds using a flame ionization detector and all halogenated test compounds using a Coulson elecrolytic conductivity detector.

All data was obtained using a purge and trap device modeled after that of Bellar and Lichtenburg[1], and constructed in our laboratory. The purging chamber dimensions are 2.5 cm by 23 cm with a medium porosity glass frit. It uses a Valco six port valve from Varian Associates (Catalog No. 57-000218-00). The trap was heated during the desorb phase by a moveable aluminum block heater maintained at 200°C. All valve changes were made manually.

Purge and Trap Efficiency

The purge and trap technique was evaluated with respect to its ability to detect 1 ppb of all the test compounds. A key factor is the purgability

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of the test compounds from aqueous solution. The recovery of test compounds from water was determined by comparing the detector response from a purge and trap analysis to that from a direct injection of the same mass of a given compound into the same chromatographic system. Except where noted, the following purge and trap conditions were employed:

Purge Time:	10-15 min
Purge Temperature:	ambient (22-25°C)
Desorb Time:	5 min
Desorb Fow Rate:	25 ml /min
Desorb Temperature:	200°C
Sample Size:	5 ml

The technique described above actually measures purge and trap recovery rather than just purging efficiency. Our results indicate that, in some cases, low recoveries are due to incomplete trapping or irreversible binding to the trap rather than incomplete purging of the test compound from water.

The purging efficiencies of all the test compounds were measured using the approach described above. Measurements were made at 10 ppb. Results for two traps are shown in Table 5. The data shows that, in some cases, recoveries determined using the Tenax/Carbosieve B (HT) trap (Trap 2) are greater than those determined using the Tenax/silica trap (Trap 1).

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Particularly noteworthy are the results for acrolein and acrylonitrile. The Trap 2 recoveries equal those obtained with Trap 1 even after increasing purging temperature and ionic strength (see Table 6). The results suggest that polymerization or irreversible absorption are the cause of low recovery, and not poor purging efficiency. Poor absorption could also possibly account for some of the low recoveries of these two compounds. In our studies, no significant improvement in recovery of acrolein and acrylonitrile was obtained even when the purging solution was heated to 50°C. There is evidence[3,4] that the increase in moisture from heating reduces the adsorptivity of acrolein and acrylonitrile on Tenax. Thus, even though high temperatures improve purgeability, the decrease in adsorptivity offsets the gain.

Compounds having a lower boiling point than trichlorofluoromethane were not trapped effectively by the Tenax/silica trap. Therefore, various Tenax/charcoal traps were prepared and tested for their ability to trap these gaseous compounds. Data obtained for Tenax/Carbosieve B (HT) traps and for Tenax/SKC charcoal traps are shown in Tables 7 and 8, respectively. For each trap, purge times of 10 and 15 min were tested.

Based upon the data shown, a number of conclusions can be drawn: a) Charcoal/Tenax traps are effective adsorbants for the compounds tested; b) Five to seven cm of charcoal are required for a retentive trap, c) Recoveries of some compounds are lower using the longer (15 min.) purge times. This indicates that gaseous compounds are easily desorbed from these traps at room temperature.

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TABLE 5. PURGE AND TRAP EFFICIENCIES OF TEST COMPOUNDS

Compound	Purge and Trap Efficiency[a]	
	Trap 1 [b]	Trap 2 [c]
trichlorofluoromethane	78	85
1,1-dichloroethylene	82	120
methylene chloride	82	140
1,2-trans-dichloroethylene	104	92
1,1-dichloroethane	100	95
chloroform	76	83
1,1,1-trichloroethane	86	108
carbon tetrachloride	60	87
trichloroethylene	77	71
1,2-dichloroethane	74	100
dichlorobromomethane	85	134
1,2-dichloropropane	83	88
1,3-trans-dichloropropylene	87	72
1,3-cis-dichloropropylene	58	60
1,1,2-trichloroethane	89	85
chlorodibromomethane	72	91
tetrachloroethylene	82	48
chlorobenzene	110	81
1,1,2,2-tetrachloroethane	28	82
bromoform	49	77
dibromomethane	93	81
2-chloroethylvinyl ether	21	45
1,2-dibromoethane	56	60
2,3-dichloropropene	87	93
1-chlorocyclohexene	68	105
p-dichlorobenzene	100	120
benzene	41	82
toluene	38	123
ethylbenzene	28	48
acrolein	9	44
acrylonitrile	15	41

6-1/2"

[a]Determined by comparing the response by purge and trap to that obtained by direct injection of the test compound.

[b]Tenax/silica trap obtained from Tekmar, Inc. Purge time, 15 min.

[c]Tenax/Carbosieve B(HT) (Supelco, Inc., Bellefonte, Pa) trap prepared in our laboratory, 14 cm Tenax + 7 cm Carbosieve B (HT). Purge time 15 min.

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TABLE 6. EFFECT OF TEMPERATURE AND IONIC STRENGTH ON PURGING EFFICIENCIES OF ACROLEIN AND ACRYLONITRILE

Compound	ng Purged	Percent Recovery			
		No Citrate Added	Citrate Added[b]		
		30°C	30°C	40°C	50°C
acrolein	99.4	8.4±0.6	14.6±1.8	13.7±1.9	11.2±1.3
acrylonitrile	104	15.0±1.2	41.9±3.6	42.1±6.6	49.6±7.6
chloroform	182	98.3±4.4	117± 30	86.±41.6	113± 11

[a]Values are the average ± standard deviation of three determinations. The percent recovery was determined by comparing purge and trap results with those obtained by direct injection of the same standard solution.

[b]Half saturated potassium citrate solution, pH 7.0.

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TABLE 7. PURGE AND TRAP RECOVERIES OF SELECTED VOLATILE ORGANOHALIDES USING CARBOSIEVE B(HT)/TENAX TRAPS

Compound	Trap #3		Trap #4		Trap #2
	10 min.	15 min.	10 min.	15 min.	15 min.
dichlorodifluoromethane	50	48	65	52	77
methyl chloride	8	2	68	79	64
vinyl chloride	53	43	93	57	100
methyl bromide	208	121	290	256	118
chloroethane	117	54	167	118	100
trichlorofluoromethane	86	36	90	50	85
1,1-dichloroethylene	84	74	88	90	120
methylene chloride	125	136	146	146	140
1,2-trans-dichloroethylene	89	85	89	91	92
1,1-dichloroethane	89	93	91	79	95
chloroform	86	91	88	86	83
1,1,1-trichloroethane	89	85	67	55	108
carbon tetrachloride	89	86	70	67	87

9-1/2"

Trap #3: 19 cm Tenax + 2 cm Carbosieve B(HT)

Trap #4: 16 cm Tenax + 5 cm Carbosieve B(HT)

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Trap #2: 14 cm Tenax + 7 cm Carbosieve B(HT)

Numbers represent percent recoveries based on a comparison with the response to the same mass by direct injection.

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TABLE 8. PURGE AND TRAP RECOVERIES OF SELECTED VOLATILE ORGANOHALIDES USING SKC CHARCOAL/TENAX TRAPS

Compound	Trap #5		Trap #6		Trap #7
	10 min.	15 min.	10 min.	15 min.	15 min.
dichlorodifluoromethane	52	20	44	39	42
methyl chloride	31	5	54	54	18
vinyl chloride	67	50	95	83	109
methyl bromide	107	45	58	48	83
chloroethane	63	32	107	95	97
trichlorofluoromethane	69	31	82	73	117
1,1-dichloroethylene	74	68	80	75	93
methylene chloride	133	133	96	94	97
1,2-trans-dichloroethylene	89	70	83	71	82
1,1-dichloroethane	81	78	86	79	93
chloroform	81	78	82	81	98
1,1,1-trichloroethane	85	78	77	72	84
carbon tetrachloride	82	72	77	82	89

8-1/2"

Trap #5: 19 cm Tenax + 2 cm SKC.

Trap #6: 16 cm Tenax + 5 cm SKC.

9-1/8"

Trap #7: 14 cm Tenax + 7 cm SKC.

Numbers represent percent recoveries based on a comparison with the response to the same mass by direct injection.

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Minimum Detection Limits

The ability of the purge and trap method to detect 1 ppb levels of all of the test compounds has been demonstrated using the flame ionization detector. All halogenated test compounds are detectable at 1 ppb by the Coulson electrolytic conductivity detector. The response of these two detectors to 1 ppb levels of all the test compounds is shown in Table 9.

In the case of the non-halogenated compounds, detection may be possible down to 0.1 ppb by FID. Many of the halogenated compounds are detectable below 0.1 ppb by Coulson. These data demonstrate the usefulness of the purge and trap method for detection of halogenated compounds at 1 ppb.

Since considerable interest exists in analyzing some of the halogenated compounds at levels below 1 ppb, selected compounds were analyzed at sub-ppb levels using the Coulson purge and trap approach. A volume of 20 ml and a purge time of 17 min were used for this study. A series of solutions, ranging from 0.1 - 10 ppb were analyzed; analyses were obtained for each level. Results are presented in Table 10.

For the compounds tested, the response over the concentration range 0.1 - 10 ppb was sufficient for analysis and demonstrated that increasing the purge volume can lower the detection limit and still yield reasonable precision. At lower concentrations, the data becomes nonlinear. Analyses at concentrations below 1-2 ppb should be performed using standard curves.

Standard Curves

In order to establish the linearity of the purge and trap technique, calibration curves were prepared for halogenated compounds by Coulson and for the aromatic and non-halogenated compounds by FID. Deionized water was spiked with the test compounds at 2, 10, 20, 40, 60, and 100 ppb and analyzed. For convenience and ease of analysis, the test compounds were divided into four groups as follows:

GROUP I	GROUP II
1,1-dichloroethane	chloroform
1,2-dichloroethane	carbon tetrachloride
1,1,1-trichlorethane	2,3-dichloropropene
1,2-dichloropropane	dibromomethane
dichlorobromomethane	trichloroethylene
1,3-trans-dichloropropylene	1,1,2-trichlorethane
1,3-cis-dichloropropylene	1,2-dibromoethane
chlorodibromomethane	bromoform
tetrachloroethylene	
1,1,2,2-tetrachloroethane	

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TABLE 9. RESPONSE IN PURGE AND TRAP ANALYSIS OF 1 PPB CONCENTRATIONS OF TEST COMPOUNDS

Compound	Peak Height Obtained at 1 ppb, div. Coulson	FID
dichlorodifluoromethane	26.4	4.5
methyl chloride	26.4	14.9
vinyl chloride	24.3	9.0
methyl bromide	6.0	3.4
chloroethane	14.0	10.5
trichlorofluoromethane	20.4	2.8
1,1-dichloroethylene	20.0	23.1
methylene chloride	49.5	10.0
1,2-trans-dichloroethylene	26.7	16.6
1,1-dichloroethane	25.6	8.6
chloroform	27.4	6.1
1,1,1-trichloroethane	20.7	16.4
carbon tetrachloride	44.8	4.7
acrolein	N/A	22.5
acrylonitrile	N/A	22.5
benzene	N/A	60.5
1,2-dichloroethane	25.9	13.5
trichloroethylene	35.0	11.5
dichlorobromomethane	40.5	7.2
2,3-dichloropropene	30.7	26.5
1,2-dichloropropane	34.8	21.5
dibromomethane	6.5	4.6
1,3-trans-dichloropropylene	21.2	10.5
2-chloroethylvinyl ether	1.2	15.5
toluene	N/A	114.0
1,3-cis-dichloropropylene	14.6	7.5
1,1,2-trichloroethane	39.6	11.5
chlorodibromomethane	20.9	3.8
1-chlorocyclohexene	8.2	31.0
tetrachloroethylene	41.0	7.5
1,2-dibromoethane	7.5	7.0
chlorobenzene	8.1	50.0
ethylbenzene	N/A	65.0
1,1,2,2-tetrachlorethane	37.0	6.0
bromoform	7.7	2.5
p-dichlorobenzene	3.2	47.0

The values shown above are the average of three analyses. Noise level was one chart division for both detectors.

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TABLE 10. ANALYSIS OF SELECTED HALOGENATED COMPOUNDS DOWN TO SUB-PPB CONCENTRATION IN 20 ML BY PURGE AND TRAP USING THE COULSON DETECTOR

Compound	Concentration Nanograms	ppb	Area	Range
chloroform	4	0.2	58	13
	10	0.5	228	13
	50	2.5	2560	90
	100	5.0	6220	270
	200	10.0	13520	1390
carbon tetrachloride	4	0.2	40	7
	10	0.5	186	9
	50	2.5	1750	10
	100	5.0	4370	420
	200	10.0	8970	2260
dichlorobromomethane	4	0.2	42	6
	10	0.5	160	25
	50	2.5	1620	60
	100	5.0	4020	160
	200	10.0	9040	610
chlorodibromomethane	4	0.2	8	2
	10	0.5	64	15
	50	2.5	706	29
	100	5.0	1870	10
	200	10.0	4490	10
bromoform	8	0.4	8	5
	20	1.0	48	6
	100	5.0	576	60
	200	10.0	1570	260
	400	20.0	4040	50
1,2-trans-dichloroethylene	4	0.2	37	13
	10	0.5	134	13
	50	2.5	1140	90
	100	5.0	2960	40
	200	10.0	6880	50
tetrachloroethylene	4	0.2	36	11
	10	0.5	158	27
	50	2.5	1500	10
	100	5.0	3600	310
	200	10.0	7100	1840

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GROUP III	GROUP IV
dichlorodifluoromethane	acrolein
methyl chloride	acrylonitrile
methyl bromide	benzene
chloroethane	toluene
1,2-trans-dichloroethylene	ethylbenzene
trichlorofluoromethene	2-chloroethylvinyl ether
1, 1-dichloroethylene	1-chlorocyclohexene
methylene chloride	chlorobenzene
	p-dichlorobenzene

Groups I, II, and III were analyzed by Coulson and Group IV was analyzed by FID.

The chromatographic conditions employed were as follows:

Column: 4m x 2mm ID glass, packed with 20% SP 2100/0.1% Carbowax 1500 on 100-120 mesh Supelcoport.

Temperature Program: Inject 40°C hold for 4 min.; program 10°C min. to 170°C; hold at 170°C for 1 min.

The purge and trap conditions were normal conditions described above. A Tenax/Carbosieve B(HT) trap (7 cm Carbosieve B) was employed.

Results of the analyses are presented graphically in Figures 1-8 for the Coulson detector and Figures 9-11 for the FID detector. From these calibration curves one can see that, in the concentration range of 1-100 ppb, the test compounds show a linear response. The data shown conform reasonably well to a linear least squares plot; in most cases the correlation coefficient is 0.99 or higher.

Evaluation of the Use of Antifoaming Agents

Samples that contain high levels of detergents or other surfactants present a difficulty for the purge and trap technique, due to foaming during the purge cycle. The foaming drives the sample out of the chamber and into the valve and transfer lines, thus contaminating the system. An alternate method of analysis, such as pentane extraction, could not be used because the same constituents causing the foaming would also cause formation of stable emulsions.

Since the presence of surfactants presents a problem for both analytical methods, three de-emulsifier formulations were obtained from Witco Chemical Corporation, Houston, Texas, to test their applicability in the above methods. The formulations were tested for their ability to prevent or reduce foaming in the purge and trap analysis.

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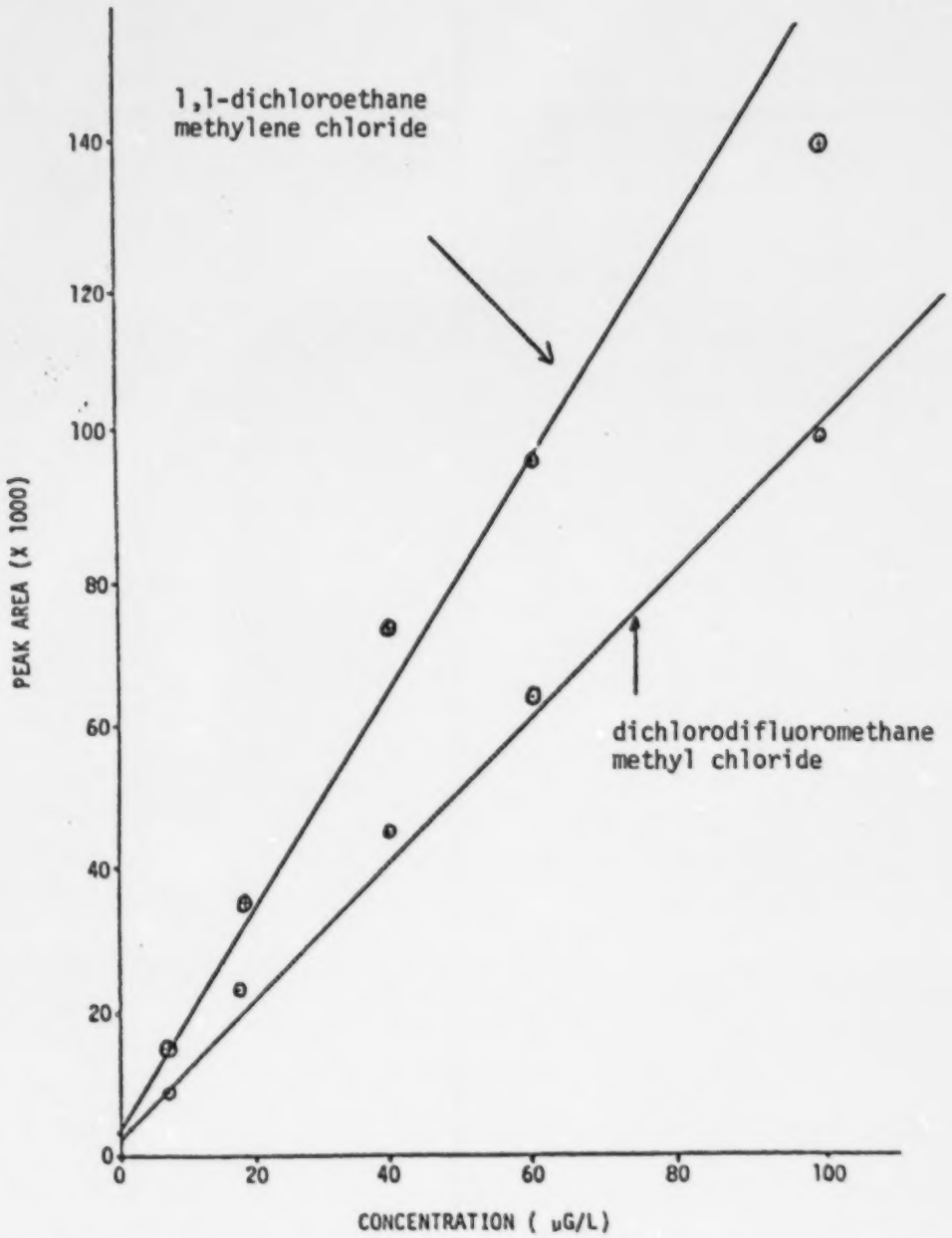

Figure 1. Standard Curves for 1,1-dichloroethane, methylene chloride dichlorodifluoromethane & methyl chloride by Coulson Purge and Trap.

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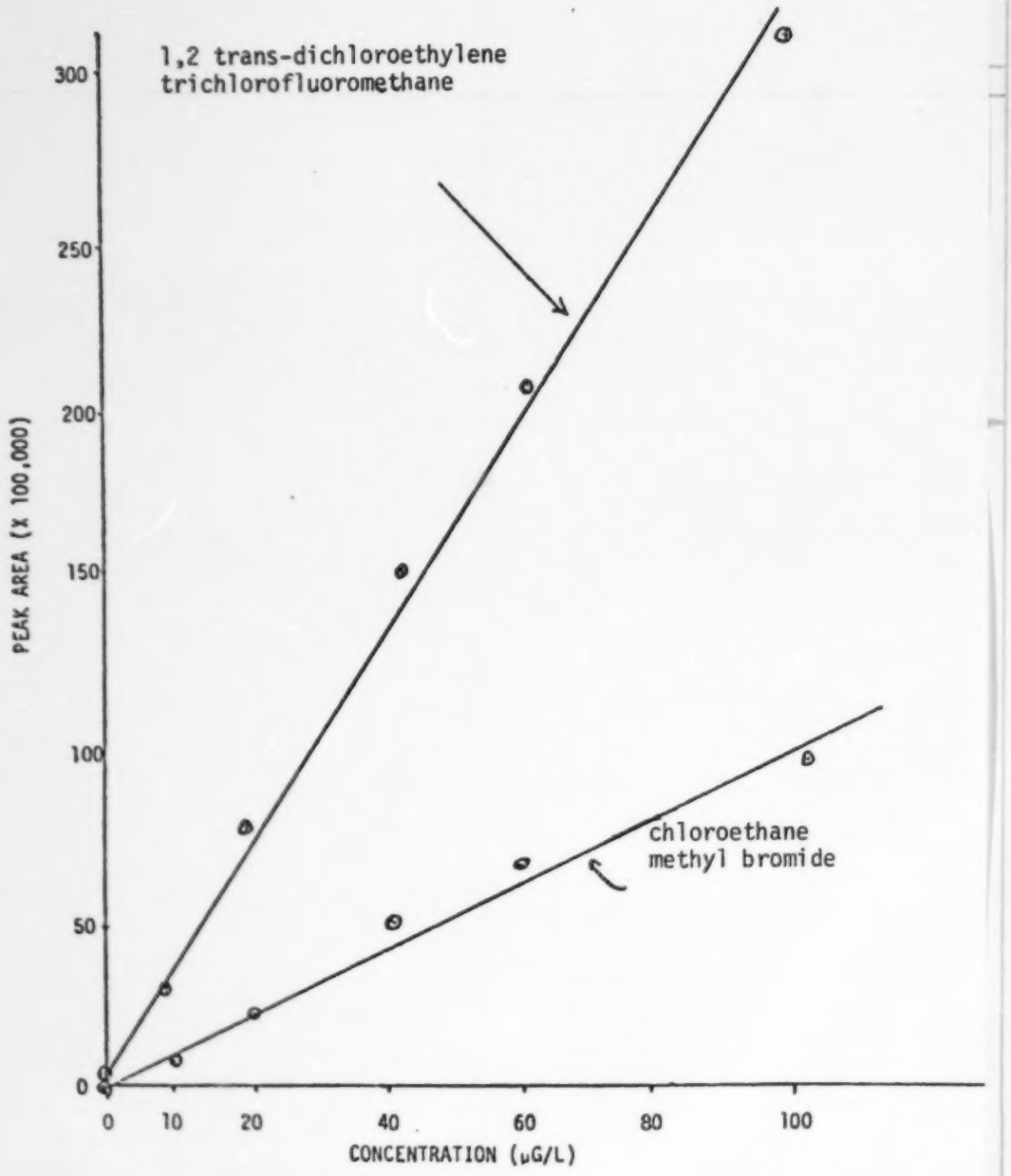

Figure 2. Standard Curves for 1,2-trans-dichloroethylene, trichlorofluoromethane, chloroethane and methyl bromide by Coulson Purge and Trap.

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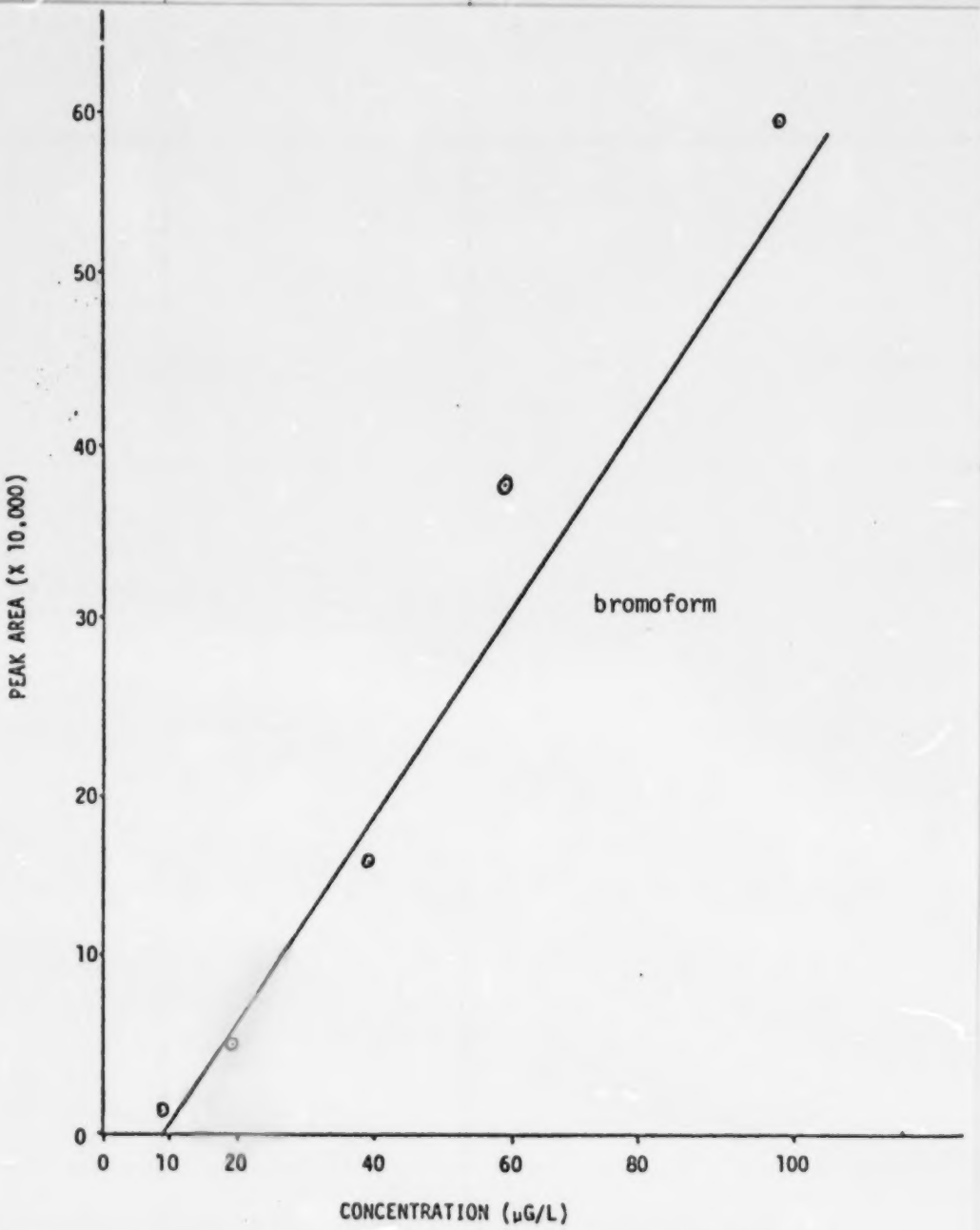

Figure 3. Standard Curves for bromoform by Coulson Purge Trap.

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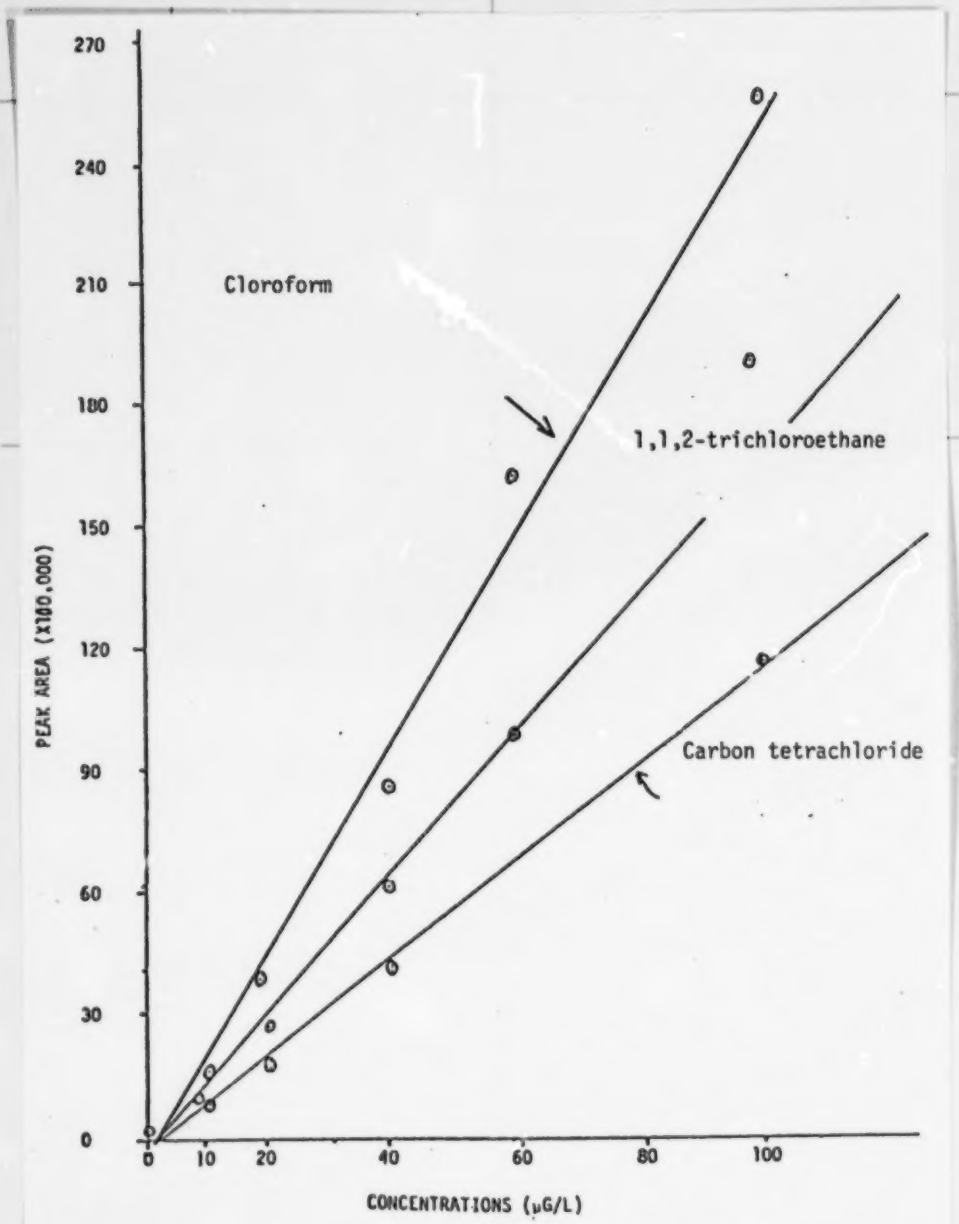

Figure 4. Standard Curves for chloroform, 1,1,2-trichloroethane and carbon tetrachloride by Coulson Purge and Trap.

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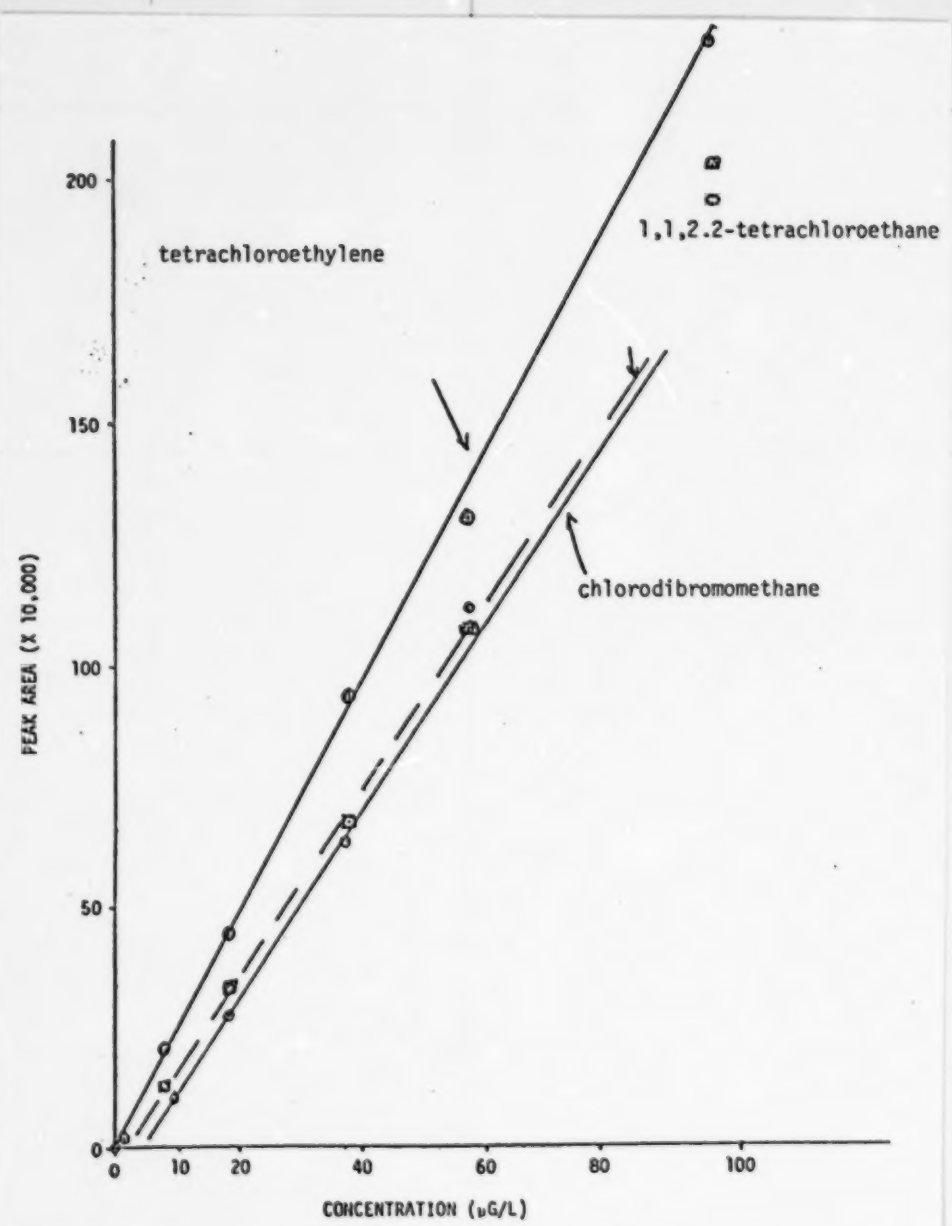

Figure 5. Standard Curves for 1,1,2,2-tetrachloroethane, tetrachloroethylene and chlorodibromomethane by Coulson Purge and Trap.

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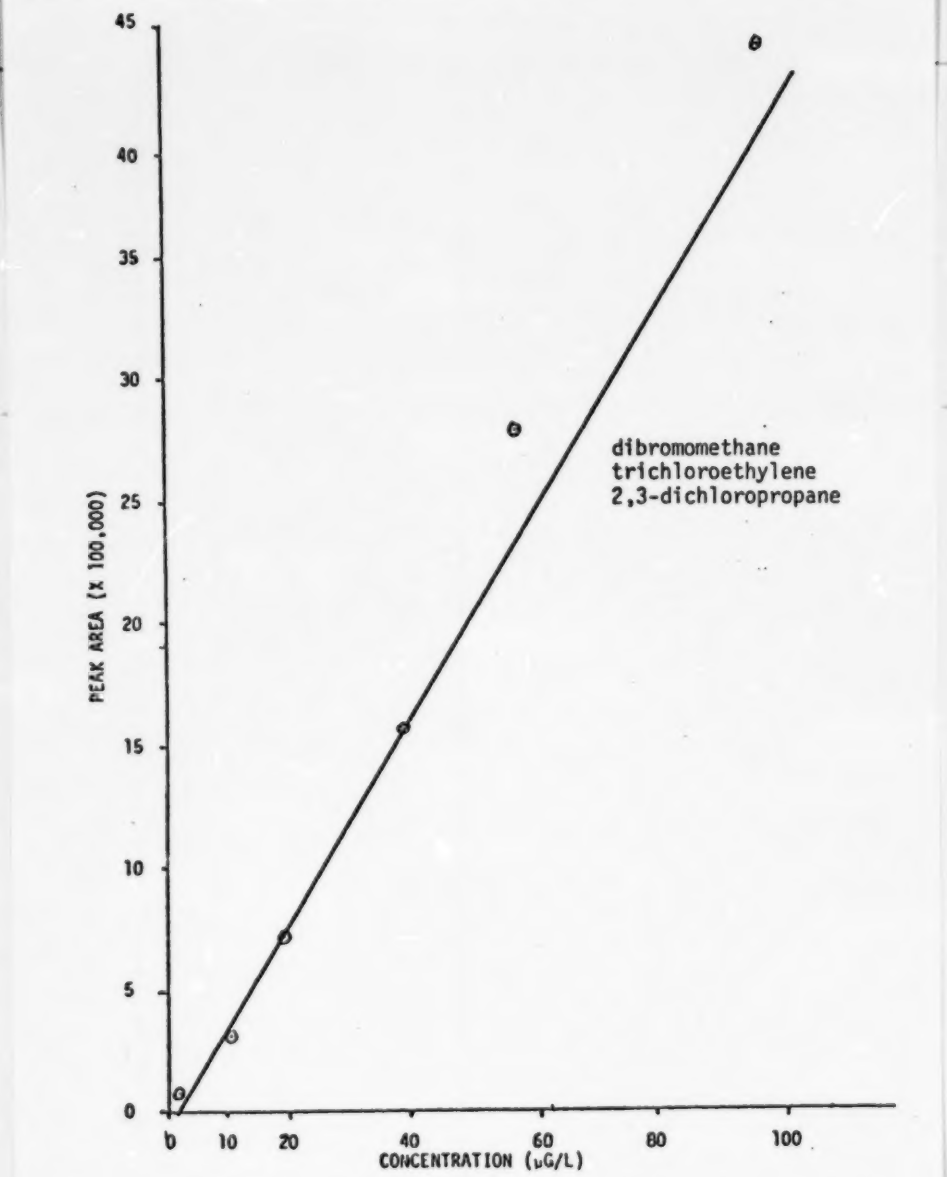

Figure 6. Standard Curves for dibromomethane, trichloroethylene and 2,3-dichloropropene by Coulson Purge and Trap.

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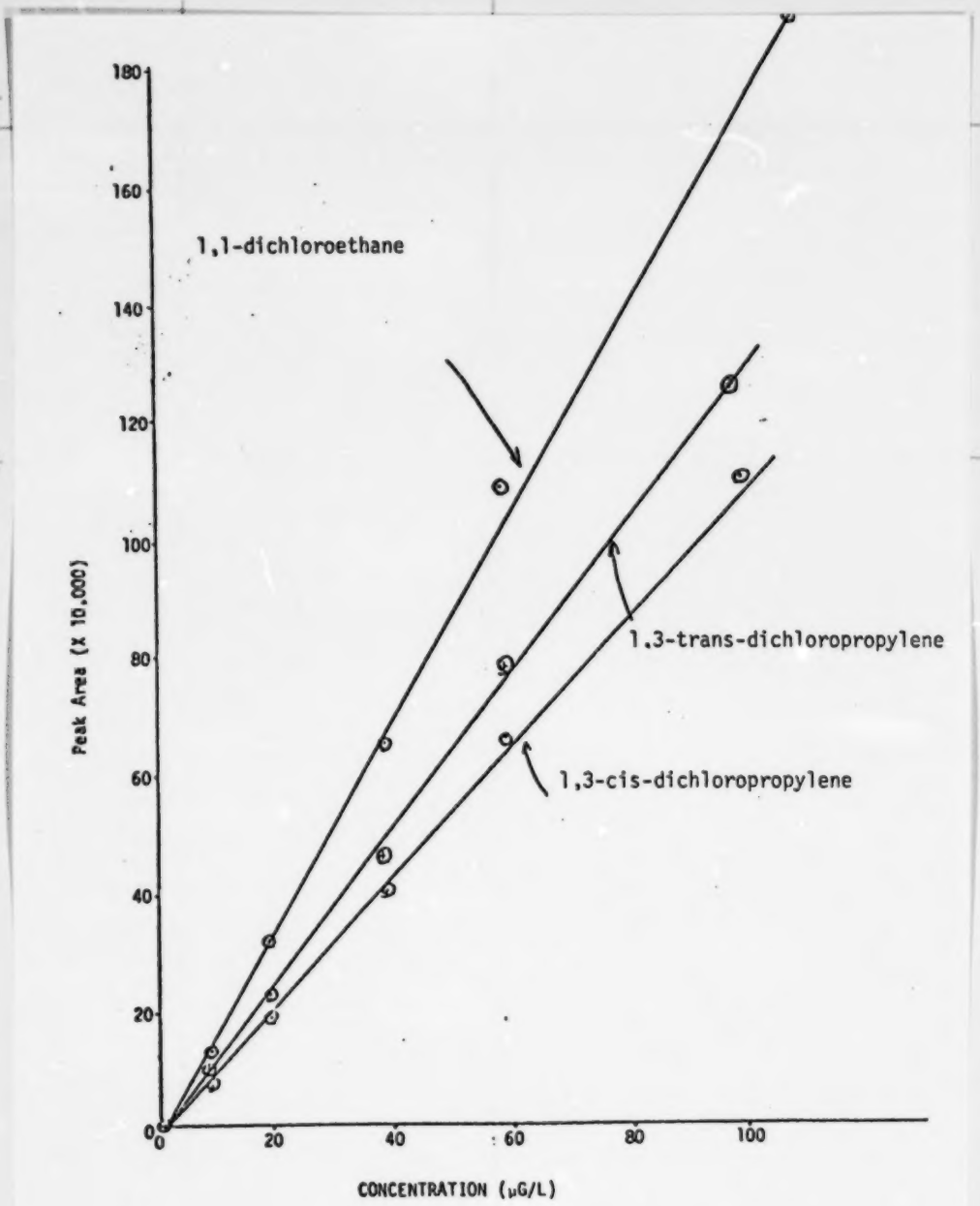

Figure 7. Standard Curves for 1,1-dichloroethane, 1,3-trans-dichloropropylene and 1,3-cis-dichloropropylene by Coulson Purge and Trap.

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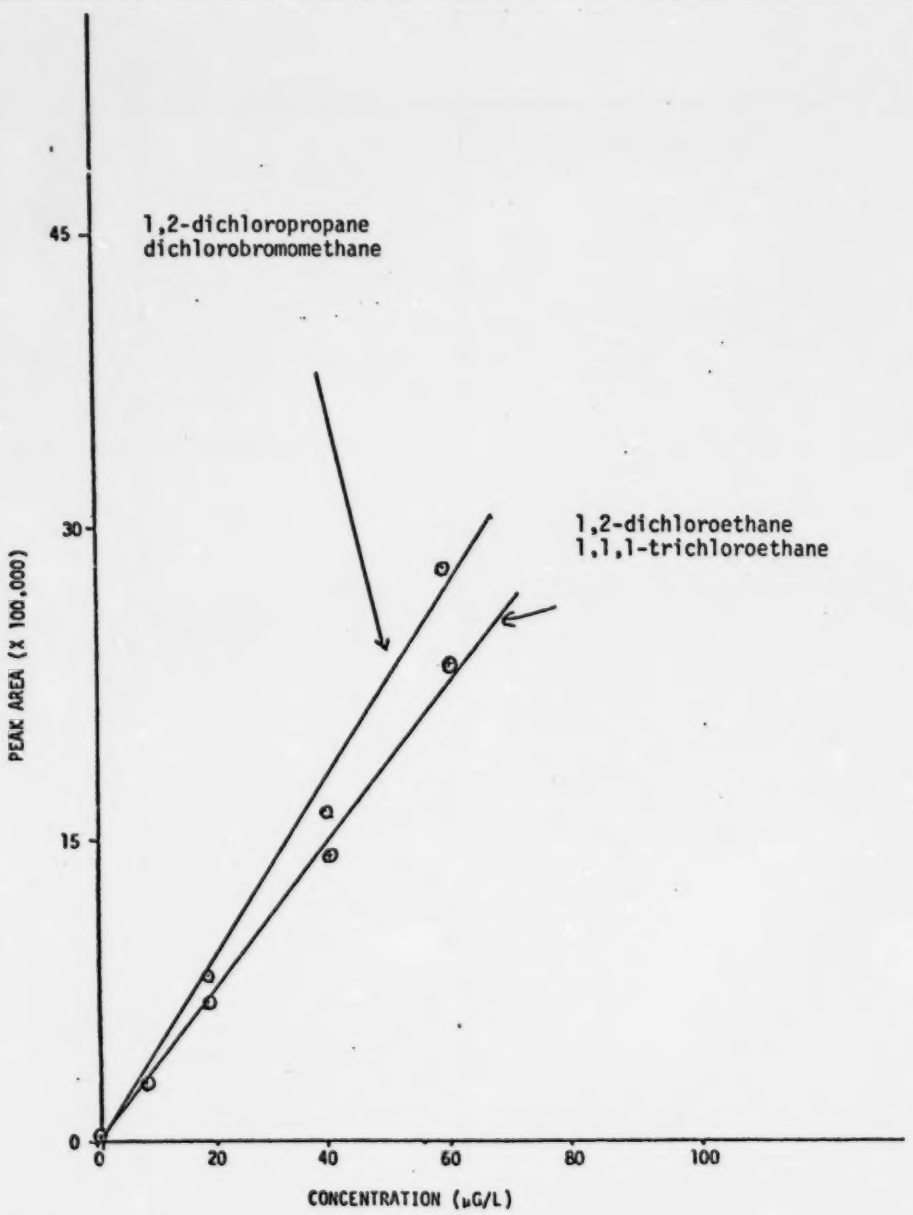

Figure 8. Standard Curves for 1,2-dichloropropane, dichlorobromomethane 1,2-dichloroethane and 1,1,1-trichloroethane by Coulson Purge and Trap.

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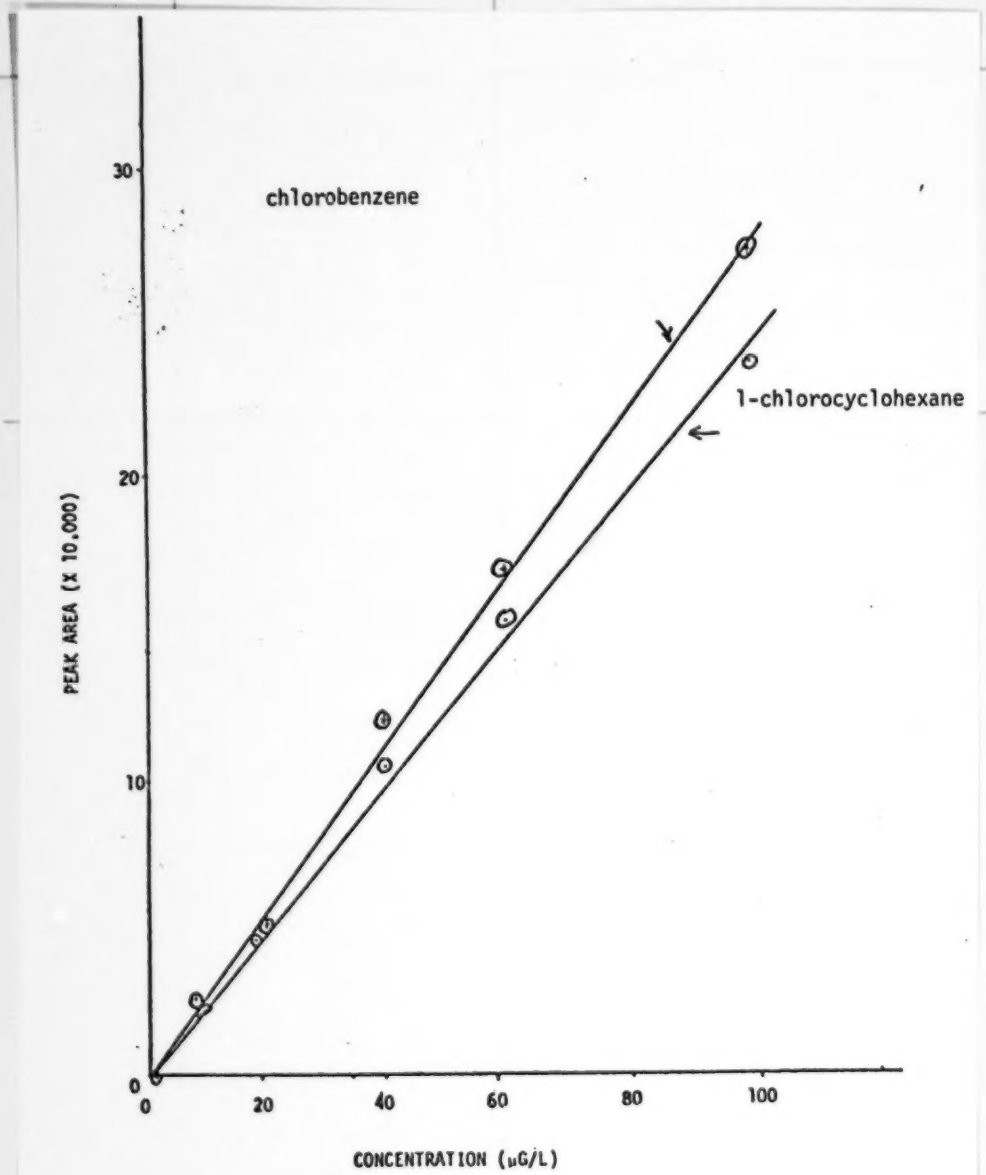

Figure 9. Standard Curve for chlorobenzene and 1-chlorocyclohexene by FID Purge and Trap.

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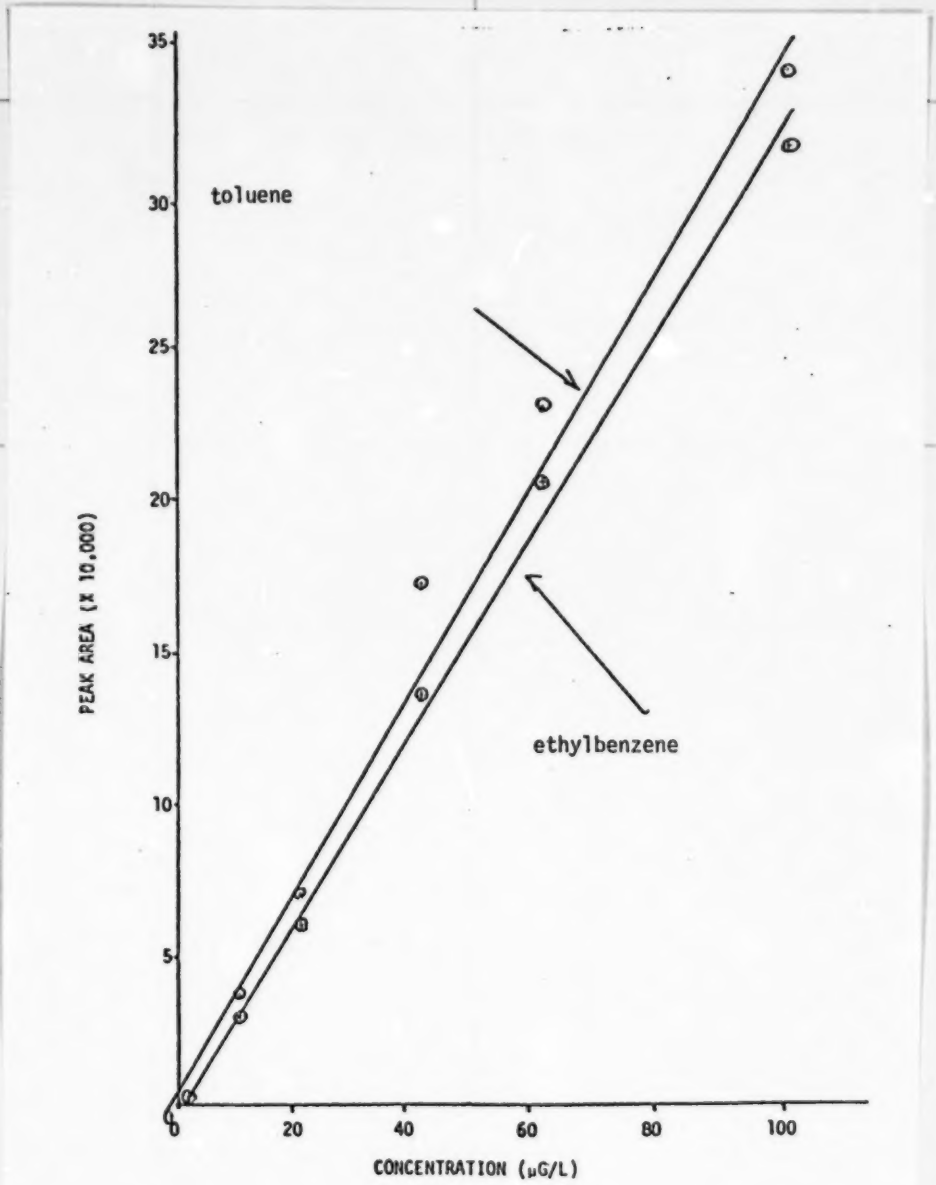

Figure 10. Standard Curves for toluene and ethylbenzene by FID Purge and Trap.

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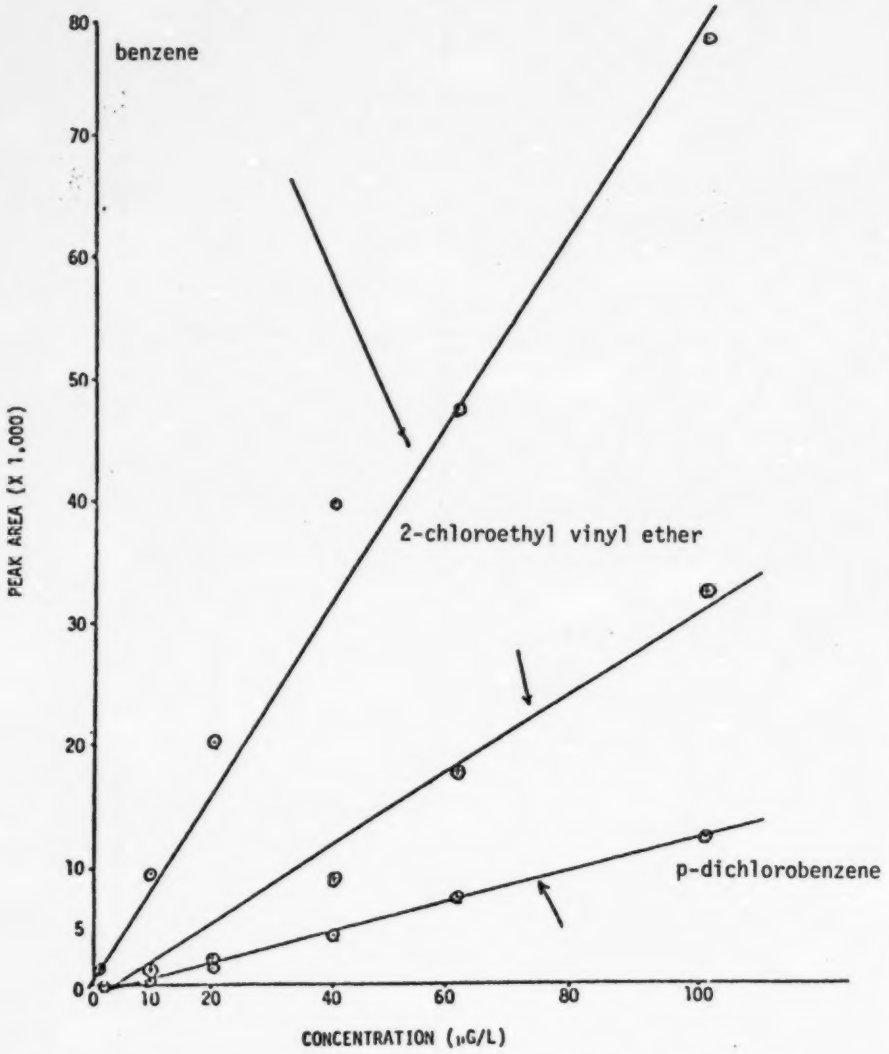

Figure 11. Standard Curves for 2-chloroethylvinyl ether, benzene and p-dichlorobenzene by FID Purge and Trap.

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Soap solutions of 0.025%, 0.05% and 0.1% were prepared using a powdered laboratory detergent and a household type liquid detergent. Five ml of each soap solution were placed in a large test tube and nitrogen gas was bubbled through at 40 ml/min. The rate of foam formation was measured in cm per min. The results of this test were that all concentrations produced over 10 cm of foam in less than one minute. In the purge chambers currently used, this rate of foam formation would be unacceptable. The same solutions were tested for foaming after adding one drop of de-emulsifier. The de-emulsifiers tested were Balab 3056A, Balab 913, and Balab 625. In every case, foaming was eliminated for periods up to ten minutes. Even a 1% detergent solution did not foam with only one drop of any of the three formulations.

The next step was to measure the effect of de-emulsifiers on the purge and trap recovery of selected compounds. First, a deionized water solution with one drop of a de-emulsifier was purged to see if the de-emulsifier contributed any volatile contaminants to the system. Each formulation was shown to be clean in this respect. A selected group of compounds was first purged from deionized water and then purged from deonized water plus one drop of each de-emulsifier. The recovery in the presence of de-emulsifier was determined relative to that from deionized water. Recovery results of average determinations using each of the three de-emulsifiers are shown in Table 11. There were no significant differences in purging efficiencies between the three de-emulsifiers.

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TABLE 11. EFFECT OF DE-EMULSIFIERS UPON THE PURGING EFFICIENCY OF SELECT COMPOUNDS

Compound	% Recovery with De-emulsifier
1,2-dichloroethane	94
dichlorobromomethane	87
1,1,2-trichloroethane	65
tetrachloroethylene	93
1-chlorocyclohexene	63
p-dichlorobenzene	10

From the above data, one can conclude that the addition of de-emulsifiers has no significant effect upon purging efficiency, except for that of the relatively nonvolatile compounds.

To test the ability of the de-emulsifiers to remove intractable emulsions in the solvent extraction method, various concentrations of detergent were shaken with pentane (35:1, V/V) to determine which concentrations would form an emulsion that was stable for at least two hours. Stable emulsions were formed with 0.5% or greater detergent.

To the stable emulsion, de-emulsifier was added one drop at a time, waiting ten minutes between drops to see if there was any separation (mixture was shaken after each addition). Although the de-emulsifiers did

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cause the pentane layer to separate out, the pentane layer was very cloudy and did not clear even after standing 24 hours. The effect of the de-emulsifier on the extraction efficiency of the test compounds was not determined.

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SOLVENT EXTRACTION/ELECTRON CAPTURE DETECTION

The purposes of this study were to determine the optimum conditions of extraction using a simple extraction procedure, then, to determine the accuracy and precision of the extraction process at the one ppb level, and to determine the suitability of the extraction solvents n-pentane and isooctane.

The first extraction techniques tested were those in which no head space was allowed in the extraction vessel. A forty ml. septum sealed vial, completely filled with an aqueous solution of the test compounds, was pierced with two 22 gauge needles. One needle was attached to a syringe containing 2 ml. of pentane. The bottle was held upside down while the pentane was injected into the vial. Through the second needle an equal volume of water was displaced from the vial, and no air was allowed to enter. The two needles were withdrawn and the vial was agitated to mix the two phases. Various methods of agitation were tested and the pentane layer analyzed by electron capture gas chromatography. The extraction efficiency for each compound was determined by comparison with standards of known concentration. The results for three agitation methods are seen in Table 12. It quickly became apparent that very vigorous agitation methods are needed to get efficient extractions when there are no headspace bubbles to help mix the two phases.

TABLE 12. EXTRACTION EFFICIENCIES OF VARIOUS MIXING METHODS FOR SOLVENT EXTRACTION

Method	Average Recovery Efficiency	Range of Recoveries
Hand Shaking Intermittent, 75 min.	30%	±8%
Mechanical Rotation, 30 RPM, 30 min.	25%	±4%
Reciprocating, 15 min. 200 cycles/min.	89%	±16%

If, on the other hand, one allows a small amount of headspace, very good extraction efficiencies can be obtained by simple hand shaking for only one minute. Trichlorofluoromethane and compounds boiling above trichlorofluoromethane could be extracted with high efficiency, as illustrated in Table 13. For those compounds boiling below trichlorofluoromethane (methyl chloride, methyl bromide, dichlorodifluoromethane, vinyl chloride, and chloroethane), which are all

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TABLE 13. EXTRACTION EFFICIENCIES AND ELECTRON CAPTURE RESPONSE CURVES FOR POLYHALOGENATED COMPOUNDS

Compound	Picograms[a] injected	Area[b] (Volt.sec)	MDL[c] (ppb)	Extraction Efficiency
	100	271		
	200	372		
dichlorodifluoromethane	500	850	1	NA
	1000	2500		
	5000	11,313		
	100	270		
	200	635		
trichlorofluoromethane	500	1320	0.8	NA
	1000	2656		
	5000	13,560		
	100	5387		
	250	5888		
chloroform	500	7679	0.3	88
	1000	11,420		
	2000	18,424		
	100	1397		
	250	4278		
1,1,1-trichloroethane	500	8,462	0.02	100
	1000	14,206		
	2000	54,126		
	100	7084		
	250	12,844		
carbon tetrachloride	500	25,390	0.02	100
	1000	39,042		
	2000	54,126		
	100	884		
	250	2198		
trichloroethylene	500	4489	0.04	97
	1000	9,690		
	2000	17,830		
	100	3071		
	250	7560		
chlorodibromomethane	500	16,093	0.1	100
	1000	24,233		
	2000	31,509		

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TABLE 13 (Continued)

Compound	Picograms[a] injected	Area[b] (Volt.sec)	MDL[c] (ppb)	Extraction Efficiency
	100	2688		
	250	5667		
dibromomethane	800	12,992	0.1	65
	1000	22,936		
	2000	34,256		
	100	792		
	250	1761		
1,1,2-trichloroethane	500	3725	0.3	91
	1000	6889		
	2000	12,450		
	100	1414		
	250	4047		
chlorodibromomethane	500	7278	0.1	100
	1000	11,891		
	2000	18,641		
	100	2296		
	250	5855		
tetrachloroethylene	500	10,144	0.02	100
	1000	18,947		
	2000	23,832		
	100	598		
	250	1374		
1,1,2,2-tetra-cholorethane	800	2452	0.04	100
	1000	4113		
	2000	7071		
	100	706		
	250	1573		
bromoform	500	3205	0.04	100
	1000	5988		
	2000	10,478		

[a]All injections were 5 microliters

[b]The detector sensitivity was 10x128, areas from HP 3352 laboratory data system.

[c]MDL = minimum detection limit; calculated as follows:

$$MDL = \frac{(Area)}{(Response\ \frac{area\ units}{gm})} \frac{(2\ ml)}{(35\ ml)\ (5\ ul)} \text{ in } \frac{gm}{ul}$$

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gases at room temperature, insufficient data was collected to determine extraction efficiency and the effect of head space. However, due to the volatility of these compounds it is expected that head space would cause variable results in analysis of these compounds by this method.

The variation in response of the electron capture detector to the test compounds is quite pronounced. For those compounds containing three or more halogens, the response is sufficiently high that one can readily detect 1 ppb or less. The monohalogenated compounds and even the dichloroethanes and dichloropropanes cause such a poor response that 100 ppb would be difficult to detect at the same detector setting used for the trihalogenated compounds. Typical response data for the more sensitive compounds are presented in Table 13. All the compounds in Table 13 can be readily detected at 1 ppb or less, assuming 100% extraction into the pentane. The detector sensitivity setting for which the minimum detection limits were calculated is not overly sensitive. Thus, even lower detection limits are possible for these compounds, if needed. For the remaining compounds, the sensitivity of the detector is relatively poor. Although one could achieve reasonable detection limits by increasing the detector sensitivity, the probability of interferences is also increased. Furthermore, if the more responsive compounds are present at detectable levels, increasing detector sensitivity will cause these compounds to saturate the detector and mask the response of less sensitive compounds.

The solvents tested were pentane and isooctane. Both were shown to be satisfactory. However, even Nanograde Quality batches from three different suppliers contained low boiling, electron capture responsive contaminants. These could not be eliminated by distillation. Furthermore, elution of the solvent normally caused a negative peak, which would interfere with quantitation of any compound eluting at the same time. Retention times of each of the solvents on each of the columns are given in Table 14. Hexane, a common solvent for electron capture work is included for comparison. As can be seen from the table, hexane masks fewer test compounds than either pentane or isooctane. Hexane offers some additional advantages over pentane and isooctane. High purity solvent is more readily available and is less expensive than the other two. Compared to pentane, hexane is more desirable because its higher boiling point makes it an easier solvent to handle; higher precision is obtained in extraction and injection. Although extraction efficiencies were not measured with isooctane and hexane, they would not be expected to differ significantly from those obtained with pentane.

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TABLE 14. COMPOUNDS MASKED BY SOLVENTS

Solvent	Column	Retention Time (min.)	Compounds Masked
pentane	1	10.6	1,1-trichloroethane
	2	9.5	carbon tetrachoride
	3	4.2	None
hexane	1	12.3	None
	2	12.1	1,3-trans-dichloropropylene
	3	7.7	None
isooctane	1	18.5	1-chlorocyclohexene
	2	16.6	None
	3	10.6	dibromomethane 1,3-trans-dichloropropylene

Note: The columns and temperature programs are the same as those described in Table 2.

MDLs for Table 13 were calculated using a minimum area of 200 units. The response was determined from the regression analysis of each curve. Further assumptions were 35 ml sample extracted with 2 ml pentane and an injection volume of 5 microliters.

Direct Aqueous Injection

Direct injection of aqueous solution of the test compounds was studied using the FID and Coulson detectors to evaluate the utility of the method in detecting the compounds at ppm levels. Using the same chromatographic columns as used for the other methods, it has been demonstrated that one can detect one ppm of almost every compound. The results are summarized in Table 15. As indicated, even the monohalogenated compounds can be detected by the Coulson at 1 ppm. Columns may require injection of blank water prior to analysis until a clean blank run is obtained, because water seems to clean the column of strongly absorbing compounds. The 20% SP 2100 column is particularly good for aqueous injection.

This method is quite applicable when the level of pollutants is around one ppm. However, there are a few problems of which one should be aware:

(a) The 0.2% carbowax 1500 column does not work well for aqueous injections. The water appears to uncover active sites which bind some compounds irreversibly and thus show a progressive loss of sensitivity during repeated runs . The other two columns do not show this behavior and appear to work better for direct aqueous injection.

(b) Occasionally unknown peaks will appear, which seem to be due to the interaction of water with the column or condensation of water in the Coulson detector transfer line between the furnace and the cell.

Both of these problems interfere with quantitation.

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TABLE 15. SUMMARY OF DIRECT INJECTION RESULTS

Compound	Retention Times (min.) Column 1	Column 2	Column 3	Response	MDL (PPM)	Detector
dichlorodifluoromethane	1.7	0.95	1.3	186	0.005	Coulson
vinyl chloride	0.7	0.54	1.8	15	0.005	Coulson
methyl chloride	-	1.0	1.6	5	10	Coulson
methyl bromide	1.4	0.8	2.2	1	1	Coulson
chloroethane	2.5	1.3	2.5	3	0.3	Coulson
trichlorofluoromethane	6.3	2.3	5.0	5	0.2	Coulson
1,1-dichloroethylene	6.9	3.6	3.4	4	0.3	Coulson
methylene chloride	4.1	4.5	3.6	10	0.1	Coulson
1,2-trans-dichloroethylene	8.8	5.2	4.7	6	0.2	Coulson
acrolein	4.7	4.2	2.5	19	0.05	FID
1.1-dichloroethane	8.2	4.5	5.6	5	0.2	Coulson
chloroform	9.3	6.7	5.9	7	0.2	Coulson
1,1,1-trichloroethane	10.9	8.8	9.2	5	0.2	Coulson
carbon tetrachloride	11.3	9.3	8.2	10	0.1	Coulson
acrylonitrile	5.4	4.8	3.2	23	0.04	FID
benzene	14.0	13.8	8.8	41	0.02	FID
1,2-dichoroethane	10.0	7.5	8.2	7	0.2	Coulson
trichloroethylene	13.6	12.7	9.9	7	0.2	Coulson
dichlorobromomethane	11.8	10.5	10.2	8	0.2	Coulson
2,3-dichloropropene	12.9	11.5	10.0	13	0.1	Coulson
1,2-dichloropropane	12.9	11.6	10.3	8	0.2	Coulson
dibromomethane	10.1	10.0	10.4	2	0.5	Coulson
1,3-trans-dichloropropylene	13.1	12.1	10.8	6	0.2	Coulson
2-chloroethylvinyl ether	15.0	14.0	10.7	2	0.4	Coulson
toluene	19.1	23.3	11.7	40	0.02	FID
1,3-cis-dichloropropylene	14.2	13.5	11.0	4	0.2	Coulson
1,1,2-trichloroethane	14.2	13.6	11.3	9	0.1	Coulson
chlorodibromomethane	14.0	13.6	12.6	5	0.2	Coulson
1-chlorocyclohexane	18.7	—	14.3	3	0.3	Coulson
tetrachloroethylene	18.1	18.3	13.4	3	0.3	Coulson
1,2-dibromoethane	14.9	14.41	12.7	3	0.3	Coulson
chlorobenzene	20.0	20.4	13.0	2	0.5	Coulson
ethylbenzene	21.8	26.7	13.7	28	0.04	FID
1,1,2,2-tetrachloroethane	18.0	18.6	14.5	5	0.2	Coulson
bromoform	16.2	16.3	14.1	2	0.5	Coulson
p-dichlorobenzene	27.3	—	17.2	0.5	2	Coulson

Column 1: 1.8 m X 2 mm glass with 1% SP1000 on Carbopack B, 60-80 mesh; Program-Inject at 50°; hold 5 min., then up 10°/min. to 225°C for 5 min.

Column 2: 1.8 m X 2 mm glass with 2% Carbowax 1500 on Carbopack C, 60-80 mesh; Program-Inject at 40°; hold 4 min., then up 10°/min. to 175°C for 10 min.

Column 3: 4 m X 2 mm glass with 20% SP2100/0.1% Carbowax 1500 on 100-125 mesh Supelcoport; Program-Inject at 50°; hold 4 min., then up 10°/min. to 170°C for 4 min.

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SECTION 4

STABILITY STUDIES

SOLVENT STABILITY STUDIES

A study was completed to determine whether concentrated solutions of the test compounds could be stored for extended periods of time without loss. The solvents selected were methanol and n-butanol. These solvents were selected because all of the test compounds are readily soluble in both; in addition, the solvents themselves are highly soluble in water.

For ease of analysis, the compounds were divided into four analytical groups, such that all the compounds in each group were separated on 1% SP1000 column. A stock solution for each group was prepared by weighing a sufficient amount of each appropriate solvent to yield a solution having 0.2-0.4 mg/ml of each compound. Twelve 40 ml screw capped vials were filled with the solution and sealed with a Teflon lined spetum. Six of the vials were stored in the refrigerator at 4°C and six were stored in a cabinet at room temperature. The concentrations of each compound in these solutions are listed in Table 16. After periods of 30, 60, and 90 days, two solutions, corresponding to the two temperatures were analyzed by gas chromatography. On the day of analysis, a fresh calibration standard was prepared in the same manner as the storage solutions. A calibration curve of three injection levels of the standard was used. Two vials from each temperature and each solvent were analyzed and the average percent remaining calculated for each compound. These results are listed in Tables 16 and 17.

The high recoveries for dibromomethane and 2-chloroethylvinyl ether in methanol are due to impurities in the solvent. The high recoveries of tetrachloroethylene and bromoform cannot be explained at this time. The high recovery of 1,2-dibromoethane in butanol is also due to the presence of solvent impurities.

It was demonstrated that, with few exceptions, all test compounds could be stored in relatively concentrated solutions in methanol or n-butanol for periods of as long as 90 days. The concentrations tested were between 0.2 and 0.4 mg/ml. All compounds tested having boiling points above that of trichlorofluoromethane can be stored in alcoholic solution in sealed containers for periods up to 60 days without significant loss (except for acrolein which is quite unstable in methanol). Between 60 and 90 days, there is some loss (15-25%) for carbon tetrachloride, toluene, trichlorofluoromethane and ethylbenzene in methanol, and for

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TABLE 16. RESULTS OF SOLVENT STABILITY STUDY IN METHANOL

	Conc. (mg/ml)	% Remaining after time indicated: 30 days 4°C	30 days R.T.	60 days 4°C	60 days R.T.	90 days 4°C	90 days R.T.
GROUP I							
trichlorofluoromethane	0.324	98	100	140	137	53	53
1,1-dichloroethylene	0.279	101	101	108	102	91	87
chloroform	0.294	70	75	104	99	100	100
1,1,1-trichloroethane	0.332	76	75	102	98	107	104
dichlorobromomethane	0.338	100	102	98	100	107	104
1,2-dichloropropane	0.281	100	101	102	95	106	99
1,1,2-trichloroethane	0.333	107	107	96	91	119	115
tetrachloroethylene	0.383	107	109	104	100	142	139
GROUP II							
methylene chloride	0.266	100	107	119	125	111	107
1,2-trans-dichloroethylene	0.262	95	102	98	111	106	104
dibromomethane	0.444	101	102	100	99	163	107
carbon tetrachloride	0.294	103	99	132	113	79	77
2,3-dichloropropene	0.531	127	116	84	90	101	95
1,3-trans-dichloropropylene	0.361	116	107	78	82	99	94
1,3-cis-dichloropropylene	0.361	109	107	44	46	99	94
GROUP III							
1,1-dichloroethane	0.330	98	84	109	106	94	86
1,2-dichloroethane	0.305	106	102	128	114	100	90
trichloroethylene	0.369	117	111	121	116	99	96
chlorodibromomethane	0.518	97	93	67	68	100	90
1,2-dibromoethane	0.435	97	90	107	106	104	100
1,1,2,2-tetrachloroethane	0.372	121	99	110	108	114	103
bromoform	0.345	98	111	112	113	134	132
GROUP IV							
acrolein	0.355	62	11	30	0	13	0
acrylonitrile	0.265	101	98	98	103	113	106
benzene	0.204	100	101	100	105	97	90
2-chloroethylvinyl ether	0.301	98	100	115	123	132	118
1-chlorocyclohexene	0.195	108	106	75	81	109	100
toluene	0.254	108	108	93	99	184	87
chlorobenzene	0.218	108	105	77	82	95	81
ethyl benzene	0.195	103	105	70	79	84	76
p-dichlorobenzene	0.306	106	113	75	84	104	95

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TABLE 17. RESULTS OF SOLVENT STABILITY STUDY IN BUTANOL

		% Remaining after time indicated					
	Conc.	30 days		60 days		90 days	
	(mg/ml)	4°C	R.T.	4°C	R.T.	4°C	R.T.
GROUP I							
trichlorofluoromethane	0.554	105	91	114	115	51	51
1,1-dichloroethylene	0.264	104	92	117	115	82	87
chloroform	0.292	121	108	135	132	110	114
1,1,1-trichloroethane	0.311	109	97	110	109	110	113
dichlorobromomethane	0.345	---	---	125	114	110	113
1,2-dichloropropane	0.242	---	---	115	112	108	104
1,1,2-trichloroethane	0.353	94	87	119	114	71	86
tetrachloroethylene	0.399	92	82	99	99	114	124
GROUP II							
methylene chloride	0.285	67	66	98	91	91	107
trans-1,2-dichloroethylene	0.271	110	109	106	103	100	114
dibromomethane	0.344	103	101	110	110	68	78
carbon tetrachloride	0.242	153	185	87	85	96	99
2,3-dichloropropene	0.596	---	---	106	104	112	116
1,3-trans-dichloropropylene	0.350	---	---	82	77	100	103
1,3-cis-dichloropropylene	0.350	105	98	86	82	100	103
GROUP III							
1,1-dichloroethane	0.478	112	128	100	94	90	77
1,2-dichloroethane	0.502	112	124	186	174	84	74
trichlorethene	0.432	---	---	122	119	102	84
chlorodibromomethane	0.477	93	100	75	75	104	92
1,2-dibromoethane	0.457	115	117	102	114	140	150
1,1,2,2-tetrachloroethane	0.325	100	109	93	92	104	93
bromoform	0.446	46	46	102	100	120	114
GROUP IV							
acrolein	0.249	100	101	182	48	88	70
acrylonitrile	0.216	98	107	76	91	84	79
benzene	0.223	158	168	---	---	90	106
2-chloroethylvinyl ether	0.248	130	138	130	126	108	103
1-chlorocyclohexene	0.234	116	124	77	76	114	118
toluene	0.285	93	100	100	99	102	109
chlorobenzene	0.262	108	116	102	103	105	119
ethyl benzene	0.237	103	111	73	72	96	103
p-dichlorobenzene	0.369	109	118	90	88	106	98

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trichloroflouromethane, 1,2-dichloropropane, 1,1,2-trichloroethane, dibromomethane, 1,2-dichloroethane, and acrylonitrile in butanol. Based on the result obtained with methanol and butanol, it seems reasonable to predict that any of the C_1 - C_4 alcohols would be satisfactory for preparing stable calibration standards of the test compounds. Other solvents may also be satisfactory.

PRESERVATION STUDY

The aim of the preservation study was to determine the effects of certain storage parameters on the integrity (i.e., chemical stability) of clean water samples containing trace levels of the test compounds at the ppb level. Parameters investigated were temperature (4°C and 25°C), pH (2, 7 and 10), and the presence of reducing agents (ascorbate, thiosulfate, and sulfite) added to destroy any residual chlorine. Samples were prepared and stored for seven days under various sets of conditions and analyzed to determine recovery of each of the compounds.

Preparation of Samples with Residual Chlorine

Residual Chlorine--

All samples were prepared to contain 2 ppm residual chlorine. A stock solution of sodium hypochlorite was used as a source of residual chlorine, assuming one hypochlorite molecule is equivalent to one chlorine molecule.

Reducing Agents—

A stock solution of each of the reducing agents was prepared such that 1.0 ml of stock solution added to 500 ml of test solution would provide sufficient reducing agent to reduce 10 ppm of residual chlorine (i.e. a five-fold excess), based on the following reactions:

$$Cl_2 + 2S_2O_3^{=} \quad 2Cl^- + S_4O_6^{=}$$

$$H_2O + Cl_2 + SO_3^{=} \quad 2Cl^- + SO_4^{=} + 2H^+$$

$$Cl_2 + C_6H_{10}O_7 \quad 2Cl^- + C_6H_8O_7 + 2H^+$$

Standards Working Solutions—

The test compounds were divided into four analytical groups in order to ensure that each compound was sufficiently separated for ease of analysis by gas chromatography. The groups are listed below.

GROUP I	GROUP II
1,1-dichloroethane	chloroform
1,2-dichloroethane	carbon tetrachloride
1,1,1-trichloroethane	trichloroethylene
dichlorobromomethane	2,3-dichloropropene
1,2-dichloroproane	dibromomethane
1,3-trans-dichloropropylene	1,1,2-trichlorethane
1,3-cis-dichloropropylene	1,2-dibromoethane

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chlorodibromomethane	bromoform
tetrachloroethene	
1,1,2,2-tetrachloroethane	
GROUP III	**GROUP IV**
dichlorodifluoromethane	acrolein
methyl chloride	acrylonitrile
vinyl chloride	benzene
chloroethane	2-chloroethylvinyl ether
methyl bromide	toluene
trichlorofluoromethene	1-chlorocyclohexene
1,1-dichloroethylene	ethylbenzene
1,2-trans-dichloroethylene	chlorobenzene
methylene chloride	p-dichlorobenzene

Group IV consists of the FID sensitive compounds and was analyzed by FID purge and trap. The other three groups were analyzed by the solvent extraction/electron capture method. Stock solutions of each group were prepared by filling a 50 ml volumetric flask almost to the mark with methanol and weighing to the nearest 0.1 mg. Fifty to 100 microliters of each compound were added and the flask reweighed and the amount recorded. After all compounds had been added, the flask was filled to the mark, stoppered and mixed. This solution was transferred to a screw capped, teflon sealed vial for storage. Twenty microliters of the stock solution was diluted to 50 ml water. This is the working standard. Ten ml of the working standard was diluted to 500 ml to form the test solution. This resulted in solutions that contained 1-20 ppb of each compound.

Preparation of Test Solutions--

Approximately one liter of purged, deionized water was adjusted to the proper pH. For pH 2, 1 N H_2SO_4 was added dropwise until the pH reached two. For pH 10, 1 N NaOH was added, and for pH7, one ml of 0.1 M phosphate buffer was added. A 500 ml volumetric flask was filled with water to within 15 ml of the mark with the pH adjusted water. One ml of the hypochlorite solution, 10.0 ml of the standards working solutions, and 1.0 ml of a preservative solution were combined, the flask filled to the mark with more purged, deionized water and the solution mixed. This solution was transferred to six 40 ml vials, leaving no head space. The vials were sealed with teflon-lined silicon rubber septa under screw caps. Three vials were stored in a refrigerator and three were stored in a cabinet at room temperature. In this manner, test solutions were prepared for each pH and reducing agent, including solutions without reducing agent.

Analysis

Groups I, II, and III were analyzed by the solvent extraction/electron capture method as described previously. Group IV was analyzed by the purge and trap/FID method. The GC packing used for the analyses was 20% SP-2100/0.1% Carbowax 1500 on 100-120 mesh Supelcoport. For Groups I and II, a 1.8 m x 2mm glass column was used, and for III and IV, a 4 m x

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2mm glass column was used. The areas of the chromatographic peaks were determined by electronic integration using a Hewlett-Packard 3352 lab data system. The results for each parameter and compound were expressed as:

$$\% \text{ Remaining after one week} = 100 \times \frac{\text{Area in Test Solution}}{\text{Area in Reference Standard}}$$

The temperature programs used were as follows:

Group I - Inject at 50°C hold 4 min ; program 10°C/min to 150°C; hold 5 min.

Group II - Inject at 40°C hold 5 min ; program 10°C/min to 150°C; hold for 3 min.

Group III - Inject at 40°C hold 6 min ; program 10°C/min to 70°C; hold for 3 min.

Group IV - Inject at 50°C hold 4 min ; program 10°C/min to 180°C; hold for 5 min.

For Group IV, the purge conditions employed were as follows:

Sample Volume	5 ml
purge flow rate	40 ml/min
purge time	10 min
desorb temp.	200°C
desorb flow	25 ml/min
desorb time	5 min

The test samples were prepared such that one group, stored at a single pH, was analyzed per day. On the day of analysis, a reference standard solution was prepared in the same manner as the samples (omitting chlorine, pH adjustment and reducing agent) and using the same standards stock solution as was used to prepare the samples. This reference standard solution was analyzed in the same manner as the test solutions.

Results

Analytical results for this study are presented in Table 18. In addition to the statistical treatment of the data presented in the next section, the following qualitative observations are offered.

1,1,2,2,-tetrachloroethane is not preserved at pH 10 under any conditions. Loss of 2-chloroethylvinyl ether occurs at pH 2 and 7. Formation of trace quantities of unidentified compounds was observed in unpreserved samples of Groups I and II. These results alone indicate the value of adding a reducing agent when collecting chlorine-treated wastewater effluents for volatile organic analyses. The value of adding a reducing reagent be even greater for actual wastewater samples which may contain many nonvolatile organics. Since it is well established that

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TABLE 18. RESULTS OF ONE WEEK STORAGE ON SAMPLE INTEGRITY

PERCENT REMAINING AFTER ONE WEEK STORAGE[a]

COMPOUND	NO PRESERVATIVE						SULFITE						THIOSULFATE						VITAMIN C					
	pH 2		pH 7		pH 10		pH 2		pH 7		pH 10		pH 2		pH 7		pH 10		pH 2		pH 7		pH 10	
	RT	C	RT	C	RT	C	RT	C	RT	C	RT	C	RT	C	RT	C	RT	C	RT	C	RT	C	RT	C
1,1-dichloro-ethane[c]	217 ±15	234 ±27	311 ±27	356 ±2	574 ±14	114 ±4	260 ±7	223 ±18	369 ±8	409 ±21	248 ±2	347 ±17	288 ±22	258 ±19	366 ±11	487 ±1	226 ±11	425 ±14	278 ±15	224 ±14	285 ±22	435 ±19	251 ±3	436 ±10
1,1,1,-trichloro-ethane[b] + 1,2-dichloro-ethane[b]	77 ±11	77 ±19	186 ±22	74 ±2	56 ±1	102 ±2	126 ±8	102 ±17	71 ±10	79 ±11	88 ±12	119 ±21	119 ±19	113 ±14	61 ±8	109 ±34	84 ±13	143 ±15	110 ±5	83 ±8	53 ±17	95 ±22	87 ±22	144 ± 6
dichlorobromo-methane[b] + 1,2-dichloro-propane[b]	89 ±7	97 ±5	122 ±14	99 ±0	46 ±13	113 ±2	106 ±3	100 ± 6	96 ±5	104 ±6	70 ±9	115 ±10	98 ±9	101 ±4	96 ±4	113 ±0	69 ±4	122 ±6	103 ±3	95 ±2	80 ±13	105 ±7	80 ±10	12 ±2
1,3-trans-dichloropropylene	0	0	0	0	46 ±13	92 ±3	55 ±3	63 ±6	42 ±0	71 ±25	37 ±0	83 ±11	0	0	0	48 ±2	0	0	41 ±6	48 ±6	41 ±0	88 ±7	51 ±17	99 ±2
1,3-cis-dichloropropylene	0	0	0	89 ±1	0	101 ±3	0	65 ±10	0	90 ±7	47 ±16	103 ±7	0	0	0	78 ±5	0	77 ±2	0	0	0	91 ±12	53 ±17	108 ±2
tetrachloro-ethylene	74 ±13	82 ±3	172 ±16	80 ±0	115 ±38	175 ±1	104 ±4	93 ±5	71 ±8	82 ±4	162 ±11	184 ±8	95 ±10	95 ±4	68 ±6	80 ±4	159 ±8	200 ±4	90 ±4	80 ±2	58 ±14	87 ±7	141 ±43	200 ±6
1,1,2,2-tetra-chloroethane	116 ±28	133 ±14	147 ±10	96 ±2	0	0	107 ±4	93 ±6	83 ±6	101 ±5	0	0	93 ±11	95 ±5	87 ±9	101 ±3	0	0	103 ±6	90 ±2	68 ±21	0	0	0

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TABLE 18 (Continued)

PERCENT REMAINING AFTER ONE WEEK STORAGE[a]

COMPOUND	NO PRESERVATIVE						SULFITE						THIOSULFATE						VITAMIN C					
	pH 2		pH 7		pH 10		pH 2		pH 7		pH 10		pH 2		pH 7		pH 10		pH 2		pH 7		pH 10	
	RT	C	RT	C	RT	C	RT	C	RT	C	RT	C	RT	C	RT	C	RT	C	RT	C	RT	C	RT	C
chloroform[c]	127 ±4	114 ±13	237 ±10	124 ±9	404 ±2	301 ±12	98 ±7	88 ±3	181 ±3	124 ±9	181 ±12	189 ±14	103 ±4	103 ±13	147 ±13	108 ±15	208 ±5	160 ±4	105 ±5	96 ±11	158 ±3	114 ±8	194 ±7	149 ±12
carbon tetrachloride	62 ±7	56 ±3	103 ±12	69 ±13	82 ±5	69 ±11	47 ±9	40 ±5	91 ±4	59 ±6	73 ±12	72 ±9	55 ±12	50 ±9	94 ±5	69 ±24	77 ±4	62 ±4	47 ±4	41 ±6	83 ±1	58 ±3	74 ±5	58 ±11
dibromomethane	99 ±3	86 ±3	127 ±21	69 ±19	81 ±7	79 ±11	106 ±5	93 ±4	101 ±15	61 ±2	91 ±20	88 ±9	109 ±13	75 ±4	83 ±5	61 ±23	96 ±33	79 ±3	98 ±3	58 ±6	83 ±1	58 ±6	78 ±5	71 ±11
trichloroethylene[b] + 2,3-dichloropropene[b]	35 ±5	83 ±2	142 ±*	80 ±5	110 ± 5	91 ±10	58 ±4	42 ±6	105 ±37	68 ±22	95 ±3	96 ±9	63 ±13	44 ±3	79 ±5	62 ±16	85 ±5	84 ±4	44 ±3	32 ±3	91 ±32	69 ±22	94 ±7	8. ±10
1,1,2-trichloroethane	82 ±3	76 ±2	90 ±3	64 ±3	33 ±5	73 ±7	81 ±4	76 ±2	83 ±1	59 ±5	34 ±14	80 ±6	80 ±8	77 ±2	119 ±9	59 ±18	36 ±2	74 ±4	79 ±2	70 ±4	82 ±3	60 ±3	58 ±4	71 ±7
1,2-dibromoethane	103 ±2	86 ±4	90 ±2	57 ±2	90 ±4	103 ±16	81 ±4	72 ±4	262 ±1	75 ±36	105 ±19	89 ±4	82 ±11	75 ±3	81 ±11	81 ±1	90 ±4	82 ±4	82 ±3	72 ±5	83 ±2	57 ±2	93 ±5	97 ±40
bromoform	113 ±2	106 ±2	90 ±2	58 ±4	90 ±2	80 ±9	83 ±5	77 ±4	85 ±0	56 ±6	87 ±7	92 ±9	83 ±11	80 ±1	82 ±3	57 ±21	87 ±4	82 ±2	83 ±3	76 ±3	82 ±2	59 ±5	90 ±5	78 ±5

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TABLE 18 (Continued)

PERCENT REMAINING AFTER ONE WEEK STORAGE[a]

COMPOUND	NO PRESERVATIVE						SULFITE						THIOSULFATE						VITAMIN C					
	pH 2		pH 7		pH 10		pH 2		pH 7		pH 10		pH 2		pH 7		pH 10		pH 2		pH 7		pH 10	
	RT	C	RT	C	RT	C	RT	C	RT	C	RT	C	RT	C	RT	C	RT	C	RT	C	RT	C	RT	C
dichloro-[b] difluoromethane	70 ±3	49 ±26	547 ±9	213 ±19	66 ±11	78 ±1	64 ±5	48 ±13	91 ±2	164 ±7	82 ±5	94 ±11	58 ±14	46 ±16	65 ±6	121 ±11	49 ±5	58 ±5	71 ±16	44 ±18	66 ±2	129 ±9	57 ±6	36 ±55
+ methyl chloride[b]																								
methyl bromide[b] + chloroethane[b]	91 ±7	23 ±15	76 ±5	108 ±8	64 ±3	83 ±4	83 ±4	57 ±4	72 ±4	97 ±1	67 ±3	92 ±4	39 ±11	45 ±8	-	49 ±3	-	39 ±4	92 ±3	16 ±43	68 ±7	93 ±4	64 ±5	67 ±13
trichloro-fluoromethane	106 ±1	45 ±1	101 ±2	107 ±0	87 ±5	92 ±0	104 ±2	77 ±2	87 ±1	95 ±1	94 ±1	99 ±2	85 ±6	76 ±6	76 ±1	84 ±2	80 ±2	82 ±2	102 ±2	58 ±26	83 ±2	87 ±2	85 ±4	49 ±61
1,1-dichloro-[b] ethylene + methylene-chloride[b]	395 ±1	266 ±2	182 ±1	231 ±1	88 ±8	100 ±7	419 ±14	381 ±1	215 ±2	218 ±1	85 ±17	100 ±8	509 ±11	475 ±3	198 ±3	206 ±2	65 ±17	70 ±3	456 ±3	359 ±18	212 ±3	212 ±1	70 ±22	49 ±17
1,2-trans-dichloro-ethylene					72 ±10	80 ±3			112 ±10	75 ±5	77 ±4	80 ±9			90 ±43	60 ±14	58 ±10	68 ±5			48 ±6		67 ±13	

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TABLE 18 (Continued)

PERCENT REMAINING AFTER ONE WEEK STORAGE[a]

COMPOUND	NO PRESERVATIVE						SULFITE						THIOSULFATE						VITAMIN C					
	pH 2		pH 7		pH 10		pH 2		pH 7		pH 10		pH 2		pH 7		pH 10		pH 2		pH 7		pH 10	
	RT	C	RT	C	RT	C	RT	C	RT	C	RT	C	RT	C	RT	C	RT	C	RT	C	RT	C	RT	C
benzene	91 ±4	83 ±4	95 ±3	88 ±5	67 ±11	71 ±10	101 ±7	93 ±9	80 ±16	81 ±2	65 ±6	64 ±4	107 ±2	97 ±4	19 ±19	77 ±10	60 ±1	55 ±4	46 ±3	66 ±1	55 ±7	67 ±0	48 ±3	53 ±1
2-chloro-ethylvinyl ether	0	0	0	0	0	113 ±56	0	0	0	0	82 ±42	54 ±25	0	0	413 ±3	0	78 ±27	96 ±45	0	0	72 ±12	72 ±29	99 ±54	80 ±26
toluene	0	15 ±6	74 ±4	92 ±8	102 ±10	102 ±17	74 ±23	64 ±72	82 ±6	82 ±0	97 ±13	86 ±9	141 ±3	126 ±3	15 ±1	80 ±5	81 ±4	81 ±3	57 ±9	151 ±80	58 ±5	71 ±4	72 ±1	71 ±2
chlorobenzene	82 ±7	73 ±3	72 ±2	82 ±2	79 ±3	82 ±7	96 ±1	76 ±2	77 ±1	80 ±2	72 ±2	72 ±4	97 ±8	86 ±1	54 ±10	76 ±5	66 ±1	63 ±1	45 ±8	58 ±2	60 ±4	67 ±2	71 ±25	61 ±1
ethylbenzene	6 ±27	19 ±26	70 ±6	86 ±1	75 ±3	86 ±9	57 ±19	63 ±4	77 ±0	79 ±1	69 ±2	68 ±5	100 ±4	88 ±2	75 ±37	70 ±3	62 ±2	56 ±2	37 ±6	58 ±5	59 ±6	65 ±2	54 ±4	55 ±8
1-chloro-cyclohexene	6 ±27	124 ±167	3 ±27	12 ±14	60 ±6	75 ±12	216 ±7	83 ±44	51 ±4	62 ±2	65 ±3	63 ±7	93 ±3	103 ±18	70 ±3	84 ±4	58 ±1	62 ±0	34 ±3	51 ±5	59 ±1	66 ±2	50 ±3	51 ±2
p-dichlorobenzene	88 ±15	76 ±4	74 ±11	480 ±85	70 ±7	96 ±34	96 ±7	81 ±4	78 ±5	84 ±1	66 ±10	66 ±1	96 ±6	94 ±2	75 ±4	76 ±4	66 ±7	60 ±3	53 ±1	66 ±6	66 ±1	72 ±1	54 ±2	62 ±1

[a] Values are the average ± the relative standard deviation of three determinations.

[b] These compounds were not separated under the chromatographic conditions employed.

[c] Solvent impurities caused chromatographic interference.

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reaction of chlorine with humic acids can produce trihalomethanes, the use of an agent to remove residual chlorine seems well advised.

The statistical analysis shows that the parameters tested are not acting independently. This is possibly due to the complexity of the solutions where different reactions can predominate as the parameters of pH, temperature, and reducing agent are varied. Obviously, much more data would have to be collected---particularly about each compounds interaction with every other---to be able to explain this anomalie more fully.

Statistical Evaluation of Preservation Study Data

Statistical analysis of the data was carried out to answer two questions: First, is any combination of conditions clearly superior for the preservation of each compound? Second, is there a set of conditions that will ensure minimal loss (30%) for a majority of the compounds?

The statistical work was performed by Dr. Wallace Etterbeek, Professor of Mathematics, California State University, Sacramento, who conducted an analysis of variance. The data was submitted as percent recoveries of test compounds after seven days storage under various conditions, called "treatment levels" in this discussion. The treatment levels are outlined in Table 19.

TABLE 19. TREATMENT LEVELS FOR PRESERVATION STUDY

Treatment Level	Preservative	pH	Temperature
1	None	2	Rm. Temp.
2	"	2	Cold
3	"	7	Rm. Temp.
4	"	7	Cold
5	"	10	Rm. Temp.
6	"	10	Cold
7	Sulphite	2	Rm. Temp.
8	"	2	Cold
9	"	7	Rm. Temp.
10	"	7	Cold
11	"	10	Rm. Temp.
12	"	10	Cold
13	Thiosulfate	2	Rm. Temp.
14	"	2	Cold
15	"	7	Rm. Temp.
16	"	7	Cold
17	"	10	Rm. Temp.
18	"	10	Cold
19	Ascorbate	2	Rm. Temp.
20	"	2	Cold
21	"	7	Rm. Temp.
22	"	7	Cold
23	"	10	Rm. Temp.
24	"	10	Cold

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The number of valid replicates at each treatement level varied from 1 to 3 and recovery percentages were obtained at all treatment levels for all compounds with the exception of 1,1,2,2-tetrachloroethane. For this compound, no recovery was obtained at pH 10.

To test for the effect of treatment level on percent recovery, the following model was used letting $\Psi_{i,j,k,l}$ represent the recovery percentage with

$i = 1,2,3,4$	Corresponding to Preservative
$j = 1,2,3$	Corresponding to pH
$k = 1,2$	Corresponding to Temperature
$l = 1,2,3$	Corresponding to Measurement Number

We assume $\Psi_{i,j,k,l} = \mu + \alpha_i + \beta_j + \gamma_k + \sigma_{i,j} + \delta_{i,k} + \rho_{j,k} + \Theta_{i,j,k} + \varepsilon_{i,j,k,l}$

Where

μ = Grand Mean

α_i = One-way Preservative Effect

β_j = One-way pH Effect

γ_k = One-way Temperature Effect

$\sigma_{i,j}$ = Two-way Preservative x pH Interaction Effect

$\delta_{i,k}$ = Two-way Preservative x Temperature Interaction Effect

$\rho_{j,k}$ = Two-way Ph x Temperature Interaction Effect

$\Theta_{i,j,k}$ = Three-way Preservative x pH x Temperature Interaction effect

and $\varepsilon_{i,j,k,l}$ is a normally distributed random variable for fixed i, j, k with mean zero and variance σ_2 .

These parameters are subject to the following conditions:

$$\sum_i \alpha_i = \sum_j \beta_j = \sum_k \gamma_k = \sum_i \sigma_{i,j} = \sum_i \delta_{i,k} = \sum_j \sigma_{i,j} = \sum_k \delta_{i,k} = \sum_j \rho_{j,k} = \sum_k \rho_{j,k} = \sum_i \Theta_{i,j,k} = \sum_j \Theta_{i,j,k} = \sum_k \Theta_{i,j,k}$$

Thus, the recovery percentages at each treatment level are assumed to be normally distributed random variables with common variance σ^2 .

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The standard three factor analysis of variance (ANOVA) provides the method for analyzing this model for one factor main effects, two factor interaction effects and three factor interaction effects. For all compounds, the analysis indicates there are, at the .05 level, significant one factor main effects and two factor interaction effects. Three factor interaction effects are significant for all compounds except bromoform, tetrachloroethylene, trichloroethylene, 2,3-dichloropropene, methylene chloride, 1,1-dichloroethane, 1,1,1-trichloroethane, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, and carbon tetrachloride. Thus, for all compounds the one factor main effects of preservative, pH and temperature on recovery are statistically significant. In addition, the analysis shows that the data cannot be explained by an additive mode since these main effects are compounded by the two factor interaction effects (preservative x pH, preservative x temperature, pH x temperature) which are statistically significant at the 0.05 significance level. These one factor and two factor interaction effects are further compounded at the 0.05 significance level in all but seven compounds by the three factor interaction effects (preservative x pH x temperature).

The remaining consideration is that of determining if any one treatment level is best for all compounds. To this end, 95 percent confidence intervals for each mean percent recovery at each treatment level are computed for each compound using a student's t distribution. This can only be done at treatment levels for which at least two measurements are recorded. Many of these confidence intervals are large due to the fact that no more than three measurements were obtained at each level. This is particularly true for treatment levels where only two measurements were available.

An arbitrary minimum of 70 percent recovery was used as a criterion for selection the best treatment. Using the mean percent recovery and the 95 percent confidences intervals three cases were considered.

Case 1. All compounds considered together. (See Table 20)

Case 2. Compounds separated into two sets.

Set A - Selected compounds (see Table 21).

Set B - Selected compounds (see Table 22).

Case 3. Three particular subsets considered. (See Table 23)

Set C - Brominated compounds

Set D - Unsaturated compounds

Set E - Aromatics

The treatment levels selected along with the mean recovery percentages and the 95% confidence intervals for each compound are given in Table 20-23.

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TABLE 20. COMPARISON OF AVERAGE RECOVERIES FOR TREATMENT LEVELS 9 AND 12

Compound	Treatment 9 Mean	Treatment 9 95% Confidence Interval	Treatment 12 Mean	Treatment 12 95% Confidence Interval
dichlorobromomethane & 1,2-dichloropropane	96	(85,104)	117	(88,145)
chlorodibromomethane	90	(75,105)	106	(77,136)
dibromomethane	98	(67,130)	88	(70,105)
1,2-dibromoethane	260	(260,260)	88	(79,98)
bromoform	85	(85,85)	92	(73,110)
tetrachloroethylene	71	(57,84)	100	(78,123)
2,3-Dichloropropene & trichloroethylene	105	(8,202)	97	(69,126)
methylene chloride & 1,1-dichloroethylene	217	(202,231)	100	(78,123)
1-chlorocyclohexene	57	(51,64)	63	(52,74)
benezene	80	(48,112)	64	(56,72)
toluene	82	(70,95)	86	(65,106)
ethylbenzene	77	(77,77)	68	(59,77)
chlorobenzene	76	(75,78)	72	(63,79)
p-dichlorobenzene	78	(68,87)	66	(66,66)
chloroform	183	(169,198)	190	(124,256)
chloroethane	72	(65,80)	92	(84,101)
1,1-dichloroethane	367	(295,438)	347	(205,488)
1,1,1-trichloroethane & 1,2-dichloroethane	71	(55,88)	117	(45,188)
1,1,2-trichloroethane	83	(82,85)	80	(68,91)
1,1,2,2-tetra-chloroethane	83	(71,96)	No Recovery	
methyl chloride & dichlorodifluoromethane	91	(87,95)	95	(64,127)
trichlorofluoromethane	87	(84,90)	58	(-29,144)
carbon tetrachloride	91	(81,100)	72	(56,88)

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TABLE 21. RECOVERY FOR SUBSET A UNDER OPTIMUM TREATMENT LEVELS

Compound	Mean	95% Confidence Interval	Mean	95% Confidence Interval
SUBSET A	Treatment 13		Treatment 12	
dichlorobromomethane & 1,2-dichloropropane	96	(45,147)	99	(93,104)
chlorodibromomethane	93	(23,162)	94	(87,101)
tetrachloroethylene	94	(18,170)	95	(85,105)
methylene chloride & 1,1-dichloroethylene	507	(361,652)	473	(435,511)
1-chlorocyclohexene	93	(85,100)	88	(84,92)
benezene	108	(103,113)	97	(88,107)
toluene	141	(133,149)	126	(113,138)
ethylbenzene	100	(90,111)	94	(91,97)
chlorobenzene	97	(79,116)	86	(84,87)
p-dichlorobenzene	96	(82,110)	103	(57,150)
1,1-dichloroethane	285	(-287,857)	260	(136,384)
1,1,1-trichloroethane & 1,2-dichloroethane	115	(-76,306)	115	(70,160)
1,1,2-trichloroethane	80	(64,96)	77	(74,81)
1,1,2,2-tetrachloroethane	93	(4,182)	95	(84,106)

TABLE 22. RECOVERY FOR SUBSET B UNDER OPTIMUM TREATMENT LEVELS

Compound	Mean	95% Confidence Interval	Mean	95% Confidence Interval
SUBSET B	Treatment 5		Treatment 9	
dibromomethane	81	(67,95)	98	(67,130)
1,2-dibromoethane	119	(9, 229)	260	(260,260)
bromoform	90	(80,101)	85	(85,85)
2,3-dichloropropene & trichloroethylene	122	(49,194)	105	(8,202)
chloroform	407	(478,435)	183	(169,198)
chloroethane	90	(88,92)	72	(65,80)
methyl chloride & dichlorodifluoromethane	79	(77,80)	91	(87,95)
trichlorofluoromethane	93	(93,93)	87	(84,90)
carbon tetrachloride	82	(71,93)	91	(81,100)

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TABLE 23. OPTIMUM TREATMENT LEVELS FOR SELECTED COMPOUNDS

Compound	Mean	95% Confidence Interval	Mean	95% Confidence Interval
SUBSET C (Brominated)	**Treatment 12**			
bromodichloromethane & 1,2-dichloropropane	116	(88,145)		
dibromochloromethane	100	(100,100)		
dibromomethane	88	(70,105)		
1,2-dibromoethane	88	(79,98)		
bromoform	92	(73,110)		
SUBSET D (Unsaturated)	**Treatment 6**			
tetrachloroethylene	177	(162,191)		
2,3-dichloropropene & trichloroethylene	91	(70,112)		
methylene chloride & 1,1-dichloroethylene	88	(71,105)		
1-chlorocyclohexene	75	(53,97)		
SUBSET E (Aromatic)	**Treatment 13**		**Treatment 12**	
benzene	108	(103,113)	97	(88,107)
toluene	141	(133,149)	126	(113,138)
ethyl benzene	100	(90,111)	94	(91,97)
chlorobenzene	97	(79,116)	86	(84,87)
p-dichlorobenzene	96	(82,110)	103	(57,150)

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Conclusions

Case 1—

Table 20 - When all compounds are considered as one group, treatment 9 is uniformly the best followed by treatment 12. With treatment 9, only 1-chlorocyclohexene with a mean recovery of 57% fell below the 70% recovery level. The 105% mean recovery for trichloroethylene and 2,3-dichloropropene is suspect because of its large confidence interval. Treatment 9 is consistently better over all compounds. Treatment 12 also provides consistent mean recoveries above 70%. It is ranked behind treatment 9 because no recoveries were recorded for 1,1,2,2-tetrachloroethane at treatment level 12.

Case 2—

When the compounds are separated into two subsets, treatment can be selected for each subset for which the mean recovery percentages were above 70% for all compounds.

Subset A (Table 21)--For this group of compounds treatment 14 produced the most consistent mean recovery percentages. Even though for most compounds the mean recovery percentages at treatment 13 were higher than those at treatment 14. The confidence intervals at treatment level 14 are much smaller than those at treatment level 13. This is particularaly true for 1,1-dichloroethane and 1,1,1-trichloroethane/1,2-dichloroethane.

Subset B (Table 22)--For this group of compounds treatment 5 produced the most consistent mean recovery percentages. (Somewhat better than treatment 9, the overall best in Case 1). The 95% confidence internal, (9,229), for 1,2-dibromomethane at treatment level 5 can be considerably reduced if this compound is placed in subset A. Using the preferred treatment 14 for subset A, the mean recovery percentage for 1,2-dibromomethane is reduced from 119% to 75% but the new 95% confidence interval is (70,80).

Case 3 (Table 23)--When certain chemically distinct groups are considered, other optimum treatment levels are obtained. The following special subsets are considered:

Subset C--Brominated Compounds. Treatment 12 gave the highest mean recovery percentages and 95% confidence intervals at or above the 70% level.

Subset D--Unsaturated Compounds. Treatment 6 gave the highest mean recovery percentages and at treatment level 6 only 1-chlorocyclohexene has a 95% confidence interval which drops below 70%.

Subset E--Aromatic Compounds. Treatment 13 gave the highest mean recovery percentages and smallest 95% confidence intervals and is ranked just ahead of treatment 14. This is the exact opposite of the ranking when these compounds are included with the other compound of subset A.

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SECTION 5

APPLICATION PHASE

The methods described in preceeding sections were tested on industrial wastewater effluents. Analysis of actual wastewater samples allows one to evaluate the effect of the presence of non-volatile organics and other dissolved solids which are typically present in wastewater. One can also evaluate the flexibility of each method in handling wide variations in concentration and number of compounds.

SELECTION AND PREPARATION OF INDUSTRIAL SAMPLES

The industrial categories used in this study were selected to give a range of difficulty in analysis. The Project Officer also requested the Category of Publicly Owned Treatment Works be included. The five industries selected were:

1. Organic Chemicals Industry (Industrial Category #12)
2. Publicly Owned Treatment Works (POTW)
3. Auto and Other Laundries (Industrial Category #19)
4. Coal Mining Industry (Industrial Category #11)
5. Pulp and Paper Industry (Industrial Category #16)

Previous work with samples from these industries indicated that their effluents contained a wide range of volatiles concentration. In each of the above industries, a number of samples were available in our laboratory. Several samples in each industry were composited to yield two liters of waste water from each industry. These samples were representative of the industry and are not typical of a single plant or treatment facility. Thus, these composited samples may represent a "worst case" for each industry.

Each composited industrial sample was analyzed five ways: (1) Direct aqueous injection using the FID; (2) Direct aqueous injection using the Coulson detector; (3) Liquid/liquid extraction with the electron capture detector; (4) Purge and Trap with the Coulson detector; and (5) Purge and trap with the FID. All the GLC data collected in the application phase were obtained using a 4mx2mm(id) glass column packed with 20% SP2100/0.1% carbowax 1500 on 100-120 mesh supelcoport.

After the initial analyses, the samples were spiked with the test compounds at 20 ppb and divided into two portions. One portion was

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analyzed immediately by purge and trap. The second portion was placed in a septum sealed 40 ml vial and placed in the refrigerator to be analyzed one week later. For ease of analysis, the test compounds were divided into four groups — such that all compounds were separated. Groups 1, 2 and 3 were analyzed using the Coulson detector; group 4 was analyzed using the FID. The groups used in the spiking phase are listed below.

GROUP I	GROUP 2
dichlorodifluoromethane	methyl chloride
methyl bromide	trichlorofluoromethane
chloroethane	chloroform
methylene chloride	carbon tetrachloride
1,2-dichloroethylene	trichloroethylene
1,1,1-trichloroethane	dibromomethane
1,2-dichloroethane	1,1,2-trichloroethane
2,3-dichloropropene	chlorodibromomethane
1,2-dichloropropane	tetrachloroethylene
	1,1,2,2-tetrachloroethane

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GROUP 3	GROUP 4
vinyl chloride	acrolein
1,1-dichloroethylene	acrylonitrile
1,1-dichloroethane	benzene
chlorbromomethane	2-chloroethylvinyl ether
1,3-trans-dichloropylene	toluene
1,3-cis-dichloroproplene	1-chlorocyclohexene
1,2-dibromoethane	chlorobenzene
bromoform	ethylbenzene
	p-dichlorobenzene

The spiked industrial samples were prepared as follows: (1) Stock solutions of each group were prepared by weighing into methanol in a 50 ml volumetric flask enough of each compound to give a concentration of 5-10 mg/ml. (2) Fifty microliters of the stock solution were diluted to 100 ml in water. This is the working solution. The stock solution was placed in a sealed vial and stored for one week to be used to make the calibration standards for the one week storage analysis. (3) One ml of the working solution was added to 250 ml of each of the industrial composites. Each spiked composite was then transferred to six 40 ml vials and sealed with a septum screw cap. A calibration standard was prepared in the same manner, using purged, deionized water. Three of the vials were placed in a refrigerator to be analyzed on the day of preparation. The results and discussion of the analyses are given in the following sections.

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ANALYSIS OF COMPOSITED SAMPLES

Direct Aqueous Injections

The results of direct aqueous injection, using both the FID and the Coulson detectors are given in Tables 24 thru 28. Peaks in the samples which matched a standard retention time within 0.1 minute were listed as positive identifications. The only other criterion used was the selectivity of the Coulson detector. For the halogenated compounds, if a peak appearing in the FID run was not confirmed by the Coulson run, then the peak was ignored. Also, for those halogenated compounds having a high FID response, both detectors had to see a peak before a quantitation was reported. Since the Coulson detector is highly selective for halogenated compounds, all peaks found by that detector which correspond to the retention time of one of the test compounds are indicated in the tables, but only those peaks which are confirmed by the FID analysis are quantitated.

It should be noted that two industrial category samples, organic chemicals and auto and other laundries, yielded a large number of peaks by FID analysis, but only a small number by Coulson analysis.

This made identification difficult in some cases. In any event, it seems certain that there are a number of volatile compounds present in these effluents, at the ppm level, which are not compounds under study here.

Analysis by Solvent Extraction and Electron Capture Detection.

The results of this analysis are found in column five of Tables 24-28. As expected, this method is capable of detecting levels of some compounds not seen by the purge and trap method. However, there are a few instances where compounds are reported at a level which should have been seen by the other methods but they were not. In general, the agreement between the extraction method and purge and trap is good.

Analysis by Purge and Trap.

Columns six and seven of Tables 24-28 contain the results of the purge and trap analyses. The same criteria for quantitation was used as in the direct injection analysis. The quantitative agreement between the two detectors is poor, but using the selectivity of the Coulson as a guide and an examination of the chromatograms indicate the FID is responding to other compounds that are present in the sample. In almost every case, the FID is measuring higher values than the Coulson, which is consistent with the above hypothesis.

ANALYSIS OF SPIKED SAMPLES

As described previously, each of the industrial composites were spiked with 20 ppb of each of the test compounds. The spiked solutions were transferred to six 40 ml glass screw capped vials and sealed with

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TABLE 24 RESULT OF ANALYSIS OF AUTO AND OTHER LAUNDRIES INDUSTRY COMPOSITED SAMPLE

Compound	Retention Time (min)	Direct Inject FID	Direct Inject Colson	Solvent Extraction EC	Purge and Trap FID	Purge and Trap Coulson
dichlorodifluoromethane	1.3					Masked
vinyl chloride	1.6					Masked
methyl chloride	1.8					Masked
methyl bromide	2.2					Masked
chloroethane	2.5					Masked
acrolein	2.5					Masked
acrylonitrile	3.2					Masked
1,2-trans-dichloroethylene	3.4					*
methylene chloride	3.6			15		*
1,2 trans-dichloroethylene	4.7					*
trichlorofluoromethane	5.0			0.1		
1,1-dichloroethane	5.6					
chloroform	5.9			30	6,800	25
carbon tetrachloride	8.2			0.7	21	0.1
1,2-dichloroethane	8.2			4	1,600	5
benzene	8.8	200				
1,1,1-trichloroethane	9.2					
trichloroethylene	9.9			7		
2,3-dichloropropene	10.0					
dichlorobromomethane	10.2			11		
1,2-dichloropropane	10.3					
dibromomethane	10.4					
2-chloroethylvinyl ether	10.7					
1,3-trans-dichloroproyene	10.8					
1,3-cis-dichloropropyene	11.0					*
1,1,2-trichloroethane	11.3					
toluene	11.7	800			580	
chlorodibromomethane	12.6				680	4
1,2-dibromoethane	12.7					
chlorobenzene	13.0					
tetrachloroethylene	13.4	53,000	97,000	202	8,300	4,200
ethylbenzene	13.7	13,000			2,600	
bromoform	14.1					*
1-chlorocyclohexene	14.3					
1,1,2,2-tetrachloroethane	14.5				134	1
p-dichlorobenzene	17.2					

All results are given in parts per billion (PPB).

*Peak detected; not quantitated.

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TABLE 25 RESULTS OF ANALYSIS OF COAL MINING INDUSTRY COMPOSITED SAMPLE

Compound	Retention Time (min)	Direct Inject		Solvent Extraction	Purge and Trap	
		FID	Colson	EC	FID	Coulson
dichlorodifluoromethane	1.3					
vinyl chloride	1.6					
methylchloride	1.8					
methylbromide	2.2					
chloroethane	2.5	60				
acrolein	2.5					
acrylonitrile	3.2					
1,1-dichloroethylene	3.4					
methylene chloride	3.6					
1,2-trans-dichloroethylene	4.7					
trichlorofluoromethane	5.0			0.3		
1,1-dichloroethane	5.6					
chloroform	5.9		7			
carbon tetrachloride	8.2		0.4			
1,2-dichloroethane	8.2					
benzene	8.8					
1,1,1-trichloroethane	9.2					
trichloroethylene	9.9		0.1			
2,3-dichloropropene	10.0					
dichlorobromomethane	10.2					
1,2-dichloropropane	10.3					
dibromomethane	10.4					
2-chloroethylvinyl ether	10.7					
1,3-trans-dichloroproylene	10.8					
1,3-cis-dichloropropylene	11.0					
1,1,2-trichloroethane	11.3					
toluene	11.7					
chlorodibromomethane	12.6					
1,2-dibromoethane	12.7					
chlorobenzene	13.0					
tetrachloroethylene	13.4					
ethylbenzene	14.1					
bromoform	14.1					
1-chlorocyclohexene	14.3					
1,1,2,2-tetrachloroethane	14.5					
p-dichlorobenzene	17.2					

All results are given in parts per billion (ppb).

*Peak detected; not quantitated.

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TABLE 26 RESULTS OF ANALYSIS OF ORGANIC CHEMICALS INDUSTRY COMPOSITED SAMPLE

Compound	Retention Time (min)	Direct Inject FID	Direct Inject Colson	Solvent Extraction EC	Purge and Trap FID	Purge and Trap Coulson
dichlorodifluoromethane	1.3				1	
vinyl chloride	1.6				Masked	
methyl chloride	1.8				Masked	
methyl bromide	2.2				Masked	Masked
chloroethane	2.5				Masked	Masked
acrolein	2.5				Masked	Masked
acrylonitrile	3.2	27,000			Masked	Masked
1,1-dichloroethylene	3.4				Masked	Masked
methylene chloride	3.6			2,000	Masked	Masked
1,2-trans-dichloroethylene	4.7				Masked	Masked
trichlorofluoromethane	5.0			5	Masked	Masked
1,1-dichloroethane	5.6				Masked	Masked
chloroform	5.9			41	Masked	90
carbon tetrachloride	8.2		700	12	1,400	1,400
1,2-dichloroethane	8.2			4	3,500	61
benzene	8.8	2,800			1,800	
1,1,1-trichloroethane	9.2					
trichloroethylene	9.9			7		
2,3-dichloropropene	10.0					
dichlorobromomethane	10.2			11		
1,2-dichloropropane	10.3					
dibromomethane	10.4				19	61
2-chloroethylvinyl ether	10.7					
1,3-trans-dichloropropylene	10.8					
1,3-cis-dichloropropylene	11.0					*
1,1,2-trichloroethane	11.3					
toluene	11.7				42	
chlorodibromomethane	12.6				42	16
1,2-dibromoethane	12.7			31		
chlorobenzene	13.0					
tetrachloroethylene	13.4	7,000	15,000		1,300	
ethylbenzene	13.7		20,000	51	1,900	1,300
bromoform	14.1				76	
1-chlorocyclohexene	14.3					
1,1,2,2-tetrachloroethane	14.5				134	1
p-pichlorobenzene	17.2	5,700	4,000		15,000	5

All results are given in parts per billion (ppb).

*Peak detected; not quantitated.

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TABLE 27 RESULTS OF ANALYSIS OF PUBLICLY OWNED TREATMENT WORKS COMPOSITED SAMPLE

Compound	Retention Time (min)	Direct Inject		Solvent Extraction	Purge and Trap	
		FID	Colson	EC	FID	Coulson
dichlorodifluoromethane	1.3					
vinyl chloride	1.6					
methyl chloride	1.8					
methyl bromide	2.2					
chloroethane	2.5	60				
acrolein	2.5					
acrylonitrile	3.2					
1,1-dichloroethylene	3.4					
methylene chloride	3.6					
1,2-trans-dichloroethylene	4.7					*
trichlorofluoromethane	5.0					
1,1-dichloroethane	5.6					
chloroform	5.9			5		9
carbon tetrachloride	8.2			0.4		
1,2-dichloroethane	8.2					
benzene	8.8	300				
1,1,1-trichloroethane	9.2					
trichloroethane	9.9			2		
2,3-dichloropropene	10.0				0.5	2
dichlorobromomethane	10.2					
1,2-dichloropropane	10.3					
dibromomethane	10.4					
2-chloroethylvinyl ether	10.7					
1,3-dichloroproylene	10.8					
1,3-cis-dichloropropylene	11.0					
1,1,2-trichloroethane	11.3					
toluene	11.7					
chlorodibromomethane	12.6					
1,2-dibromoethane	12.7					
chlorobenzene	13.0					
tetrachloroethylene	13.4			11	11	9
ethylbenzene	13.7					
bromoform	14.1					
1-chlorocyclohexene	14.3					
1,1,2,2-tetrachloroethane	14.5					
p-dichlorobenzene	17.2					

All results are given in parts per billion (ppb).

*Peak detected; not quantitated.

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TABLE 28 RESULTS OF ANALYSIS OF PULP AND PAPER INDUSTRY COMPOSITED SAMPLE

Compound	Retention Time (min)	Direct Inject		Solvent Extraction	Purge and Trap	
		FID	Colson	EC	FID	Coulson
dichlorodifluoromethane	1.3					
vinyl chloride	1.6					
methyl chloride	1.8					
methyl bromide	2.2					
chloroethane	2.5	200				
acrolein	2.5					
acrylonitrile	3.2					
1,1-dichloroethylene	3.4					
methylene chloride	3.6		700	106	12	61
1,2-trans-dichloroethene	4.7					*
trichlorofluoromethane	5.0					
1,1-dichloroethane	5.6					
chloroform	5.9			19		12
carbon tetrachloride	8.2			0.4		
1,2-dichloroethane	8.2					
benzene	8.8					
1,1,1-trichloroethane	9.2					
trichloroethane	9.9			0.1		0.1
2,3-dichloropropene	10.0					
dichlorobromomethane	10.2					
1,2-dichloropropane	10.3					
dibromomethane	10.4					
2-chloroethylvinyl ether	10.7					
1,3-trans-dichloropropylene	10.8					
1,3-cis-dichloropropylene	11.0					
1,1,2-trichloroethane	11.3					
toluene	11.7					
chlorodibromomethane	12.6					
1,2-dibromoethane	12.7					
chlorobenzene	13.0					
tetrachloroethylene	13.4			0.6		
ethylbenzene	13.7				1	
bromoform	14.1					
1-chlorocyclohexene	14.3					
1,1,2,2-tetrachloroethane	14.5					
p-dichlorobenzene	17.2					

All results are given in parts per billion (ppb).

*Peak detected; not quantitated.

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Teflon lined silicon rubber septums. Three of these vials were analyzed by Purge and Trap immediately and three were stored in a refrigerator for one week, then analyzed. The results are seen in Tables 29 thru 33. The concentration shown for the spiked compounds are the average of three determinations ± the relative standard deviation.

The gasses dichlorodifluoromethane, methyl chloride, methyl bromide and chloroethane were not seen, probably due to a very rapid loss from the working solution. In order to see these compounds, an alternative spiking procedure must be used. However, their rapid loss strongly suggests that they are not likely to be found in an industrial effluent unless sampling is done very soon after the gases enter the effluent.

In general, the precision of analysis was poor. One significant factor was the frequent presence of interfering compounds and the occasional high levels of some test compounds in the sample prior to spiking. These situations caused sufficient skewing or distortion of the chromatograms such that correct integration of peaks was not accomplished. It was usually not possible to check peak heights against integrator values, but in the few instances where it was possible, the precision was usually within 10% relative standard deviation. A second factor is the carryover between replicate runs. High levels of some compounds made carryover a significant problem. Due to time constraints, blanks were not run between replicates, but only between different samples.

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TABLE 29 ANALYSIS OF AUTO AND OTHER LAUNDRIES INDUSTRY SPIKED SAMPLE

Compound	Reten. time (min.)	Spike level (ppb)	Concentration Determined (ppb) Back-ground	Spiked Day 0	Spiked Day 7
dichlorodifluoromethane	1.3	30.7	Masked	Masked	Masked
methyl chloride	1.8	26.9	"	"	"
methyl bromide	2.2	33.1	"	"	"
chloroethane	2.5	28.0	"	"	"
acrolein*	2.5	33.6	"	"	"
acrylonitrile*	3.2	17.0	"	"	"
1,1-dichloroethylene	3.4	23.8	"	"	"
methylene chloride	3.6	21.2	"	79±8%	90±1%
1,2-trans-dichloroethylene	4.7	21.4	"	42±12%	27±1%
trichlorofluoromethane	5.0	14.9	"	20±21%	18±0%
1,1-dichloroethane	5.6	20.8	"	20±7%	18±8%
chloroform	6.9	24.0	25	69±28%	32±38%
carbon tetrachloride	8.2	17.9	0.1	30	12
1,2-dichloroethane	8.2	20.2	5	28±45%	22±4%
benzene*	8.8	22.0	50	130±8%	116±6%
1,1,1-trichloroethane	9.2	22.6		55±10%	12±2%
trichloroethylene	9.0	23.0		17±74%	36±33%
2,3-dichloropropene	10.0	20.0		44±23%	17±4%
dichlorobromomethane	10.2	21.4		22±28%	20±19%
1,2-dichloropropane	10.3	22.4		44±23%	17±4%
dibromomethane	10.4	20.0		61±74%	27±33%
2-chloroethylvinyl ether*	10.7	20.0		22±19%	29±26%
1,3-trans-dichloropropylene	10.8	11.9		8±12%	4±90%
1,3-cis-dichloropropylene	11.0	11.9		5±65%	31±77%
1,1,2-trichloroethane	11.3	25.0		48±55%	38±80%
toluene*	11.7	22.8	580	858±5%	694±1%
chlorodibromomethane	12.6	26.6	4	107±38%	195±52%
1,2-dibromoethane	12.7	23.6	Masked	Masked	Masked
chlorobenzene*	13.0	21.4	"	"	"
tetrachloroethylene	13.4	20.8	"	"	"
ethylbenzene	13.7	19.9	"	"	"
bromoform	14.1	19.9	"	"	"
1-chlorocyclohexene*	14.3	20.0	"	"	"
1,1,2,2-tetrachloroethane	14.5	20.8	"	"	"
p-dichlorobenzene*	17.2	20.6	"	"	"

* These compounds were analyzed using the FID. All others were analyzed using Coulson Detector.

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TABLE 30 ANALYSIS OF COAL MINING INDUSTRY SPIKED SAMPLE

Compound	Reten. time (min.)	Spike level (ppb)	Concentration Determined (ppb) Back-ground	Spiked Day 0	Spiked Day 7
dichlorodifluoromethane	1.3	30.7			
methyl chloride	1.8	26.9			
methyl bromide	2.2	33.1			
chloroethane	2.5	28.0			
acrolein*	2.5	33.6		22±31%	20±17%
acrylonitrile*	3.2	17.0		14±8%	11±23%
1,1-dichloroethylene	3.4	23.8		27±1%	15±36%
methylene chloride	3.6	21.2		62±13%	76±8%
1,2-trans-dichloroethylene	4.7	21.4		28±1%	27±21%
trichlorofluoromethane	5.0	14.9		Masked	Masked
1,1-dichloroethane	5.6	20.8		20±2%	35±4%
chloroform	6.9	24.0		25±10%	22±18%
carbon tetrachloride	8.2	17.9		16±10%	14±29%
1,2-dichloroethane	8.2	20.2		24±21%	20±7%
benzene*	8.8	22.0		18±37%	15±55%
1,1,1-trichloroethane	9.2	22.6		21±36%	13±13%
trichloroethylene	9.0	23.0		22±5%	14±20%
2,3-dichloropropene	10.0	20.0		20±4%	16±10%
dichlorobromomethane	10.2	21.4		20±6%	44±12%
1,2-dichloropropane	10.3	22.4		20±4%	16±10%
dibromomethane	10.4	20.0		17±1%	12±20%
2-chloroethylvinyl ether*	10.7	20.0		13±17%	12±21%
1,3-trans-dichloropropylene	10.8	11.9		12±8%	20±7%
1,3-cis-dichloropropylene	11.0	11.9		9±6%	22±39%
1,1,2-trichloroethane	11.3	25.0		26±5%	27±9%
toluene*	11.7	22.8		18±15%	13±14%
chlorodibromomethane	12.6	26.6		27±6%	13±22%
1,2-dibromoethane	12.7	23.6		24±17%	21±4%
chlorobenzene*	13.0	21.4		15±15%	12±13%
tetrachloroethylene	13.4	20.8		16±7%	6±15%
ethylbenzene	13.7	19.9		13±15%	9±13%
bromoform	14.1	19.9		23±10%	74±8%
1-chlorocyclohexene*	14.3	20.0		14±14%	10±10%
1,1,2,2-tetrachloroethane	14.5	20.8		21±1%	20±9%
p-dichlorobenzene*	17.2	20.6		10±19%	8±13%

* These compounds were analyzed using the FID. All others were analyzed using Coulson Detector.

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TABLE 31 ANALYSIS OF ORGANIC CHEMICALS INDUSTRY SPIKED SAMPLE

Compound	Reten. time (min.)	Spike level (ppb)	Concentration Determined (ppb) Back-ground	Spiked Day 0	Spiked Day 7
dichlorodifluoromethane	1.3	30.7	Masked		
methyl chloride	1.8	26.9	"		
methyl bromide	2.2	33.1	"		
chloroethane	2.5	28.0	"		
acrolein*	2.5	33.6	"	600±38%	536±28%
acrylonitrile*	3.2	17.0	"	71±15%	3853±15%
1,1-dichloroethylene	3.4	23.8	"	Masked	Masked
methylene chloride	3.6	21.2	"	"	"
1,2-trans-dichloroethylene	4.7	21.4	"	"	"
trichlorofluoromethane	5.0	14.9	"	"	"
1,1-dichloroethane	5.6	20.8		"	"
chloroform	6.9	24.0	90	63±35%	14±34%
carbon tetrachloride	8.2	17.9	1400	81	101
1,2-dichloroethane	8.2	20.2	61	13800±3%	5002
benzene*	8.8	22.0	1800	1559±4%	1553±2%
1,1,1-trichloroethane	9.2	22.6		Masked	Masked
trichloroethylene	9.0	23.0		56±24%	142±33%
2,3-dichloropropene	10.0	20.0		32±28%	96±28%
dichlorobromomethane	10.2	21.4		150±17%	27±2%
1,2-dichloropropane	10.3	22.4		32±28%	96±28%
dibromomethane	10.4	20.0	61	48±24%	108±33%
2-chloroethylvinyl ether*	10.7	20.0		169±30%	63±5%
1,3-trans-dichloropropene	10.8	11.9		Masked	Masked
1,3-cis-dichloropropene	11.0	11.9		9	1
1,1,2-trichloroethane	11.3	25.0		10±3%	25±73%
toluene*	11.7	22.8	42	98±10%	74±2%
chlorodibromomethane	12.6	26.6	16	Masked	Masked
1,2-dibromoethane	12.7	23.6		"	"
chlorobenzene*	13.0	21.4	1300	"	"
tetrachloroethylene	13.4	20.8	1300	"	"
ethylbenzene	13.7	19.9	76	"	"
bromoform	14.1	19.9		"	"
1-chlorocyclohexene*	14.3	20.0		"	"
1,1,2,2-tetrachloroethane	14.5	20.8		"	"
p-dichlorobenzene*	17.2	20.6	5	"	"

* These compounds were analyzed using the FID. All others were analyzed using Coulson Detector.

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TABLE 32 ANALYSIS OF PUBLICILY OWNED TREATMENT WORKS SPIKED SAMPLE

Compound	Reten. time (min.)	Spike level (ppb)	Concentration Determined (ppb) Back-ground	Spiked Day 0	Spiked Day 7
dichlorodifluoromethane	1.3	30.7			
methyl chloride	1.8	26.9			
methyl bromide	2.2	33.1			
chloroethane	2.5	28.0			
acrolein*	2.5	33.6		20±58%	18±67%
acrylonitrile*	3.2	17.0		6±16%	109±59%
1,1-dichloroethylene	3.4	23.8		40±16%	16±48%
methylene chloride	3.6	21.2		70±7%	83±41%
1,2-trans-dichloroethlyene	4.7	21.4		31±13%	11±111%
trichlorofluoromethane	5.0	14.9		Masked	Masked
1,1-dichloroethane	5.6	20.8		21±11%	38±3%
chloroform	6.9	24.0	9	35±2%	30±5%
carbon tetrachloride	8.2	17.9		21±4%	11±3%
1,2-dichloroethane	8.2	20.2		33±7%	15±29%
benzene*	8.8	22.0		36±38%	20±39%
1,1,1-trichloroethane	9.2	22.6		25±19%	10±34%
trichloroethylene	9.0	23.0		21±1%	16±14%
2,3-dichloropropene	10.0	20.0		20±17%	12±9%
dichlorobromomethane	10.2	21.4	2	22±3%	45±3%
1,2-dichloropropane	10.3	22.4		20±17%	12±9%
dibromomethane	10.4	20.0		29±1%	14±14%
2-chloroethylvinyl ether*	10.7	20.0		13±24%	13±7%
1,3-trans-dichloroproplyene	10.8	11.9		12±4%	19±29%
1,3cis-dichloropropylene	11.0	11.9		10±8%	16±44%
1,1,2-trichloroethane	11.3	25.0		28±3%	27±1%
toluene*	11.7	22.8	0.5	19±101%	11±7%
chlorodibromomethane	12.6	26.6		30±2%	13±9%
1,2-dibromoethane	12.7	23.6		19±7%	49±2%
chlorobenzene*	13.0	21.4		11±22%	5±6%
tetrachloroethylene	13.4	20.8	9	36±4%	15±1%
ethyl benzene	13.7	19.9		1±16%	0.2±0%
bromoform	14.1	19.9		20±12%	71±20%
1-chlorocyclohexene*	14.3	20.0		12±18%	11±6%
1,1,2,2-tetrachloroethane	14.5	20.8		24±0%	20±27%
p-dichlorobenzene*	17.2	20.6		17±16%	16±2%

* These compounds were analyzed using the FID. All others were analyzed using Coulson Detector.

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TABLE 33 ANALYSIS OF PUMP AND PAPER INDUSTRY SPIKED SAMPLE

Compound	Reten. time (min.)	Spike level (ppb)	Concentration Determined (ppb) Back-ground	Spiked Day 0	Spiked Day 7
dichlorodifluoromethane	1.3	30.7			
methyl chloride	1.8	26.9			
methyl bromide	2.2	33.1			
chloroethane	2.5	28.0			
acrolein*	2.5	33.6		29±36%	28±40%
acrylonitrile*	3.2	17.0		130±10%	119±6%
1,1-dichloroethylene	3.4	23.8		178±5%	19±30%
methylene chloride	3.6	21.2	61	1900±11%	302±8%
1,2-trans-dichloroethylene	4.7	21.4		4±34%	Masked
trichlorofluoromethane	5.0	14.9		Masked	Masked
1,1-dichloroethane	5.6	20.8		74±7%	100±6%
chloroform	6.9	24.0	12	40±4%	44±3%
carbon tetrachloride	8.2	17.9		17±8%	15±4%
1,2-dichloroethane	8.2	20.2		17±15%	14±26%
benzene*	8.8	22.0		114±2%	118±3%
1,1,1-trichloroethane	9.2	22.6		13±14%	6±13%
trichloroethylene	9.0	23.0	0.1	23±5%	17±14%
2,3-dichloropropene	10.0	20.0		16±16%	12±8%
dichlorobromomethane	10.2	21.4		25±13%	46±1%
1,2-dichloropropane	10.3	22.4		16±16%	12±8%
dibromomethane	10.4	20.0		19±11%	15±14%
2-chloroethylvinyl ether*	10.7	20.0		13±23%	14±2%
trans-1,3-dichloropropene	10.8	11.9		14±19%	19±11%
1,3-cis-dichloropropylene	11.0	11.9		10±1%	25±30%
1,1,2-trichloroethane	11.3	25.0		24±2%	29±7%
toluene*	11.7	22.8		20±12%	20±2%
chlorodibromomethane	12.6	26.6		28±3%	15±15%
1,2-dibromoethane	12.7	23.6		26±55%	23±11%
chlorobenzene*	13.0	21.4		17±14%	18±2%
tetrachloroethylene	13.4	20.8		18±4%	12±11%
ethylbenzene	13.7	19.9		17±13%	17±7%
bromoform	14.1	19.9		25±8%	90±7%
1-chlorocyclohexene*	14.3	20.0		17±13%	17±2%
1,1,2,2-tetrachloroethane	14.5	20.8		20±6%	22±11%
p-dichlorobenzene*	17.2	20.6		17±16%	16±10%

* These compounds were analyzed using the FID. All others were analyzed using Coulson Detector.

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SECTION 6

PROPOSED ANALYTICAL SCHEME

PREPARATION OF CALIBRATION STANDARDS

Since the results of our stability study indicate that alcoholic solutions of the test compounds in the mg/ml range are stable over a period of 90 days, it is recommended that stock solutions in the 0.2 - 0.4 mg/ml range to be prepared of all compounds to be determined. Most of the test compounds can be made up in methanol; acrolein and carbon tetrachloride are more stable in n-butanol. In any case, a highly pure solvent is necessary. It is our experience that even nanograde or pesticide grade solvents often contain low boiling impurities.

Stock solutions can be prepared by filling a 50 ml volumetric flask almost to the mark with methanol, or other alcohol, stoppering and weighing to the nearest 0.1 mg. Remove the flask from the balance and add 15-30 microliters of test compound; stopper and reweigh. Other compounds may be added to the same solution if desired. Fill to the mark with solvent and mix well. Aqueous standards in the ppb range can be readily obtained by diluting 20-50 microliters of the stock solution to 100-1000 ml.

Stock solutions of the gases can be made in a similar fashion, but their stability is much less certain. Methanol and isooctane solutions of dichlorodifluoromethane were stored in the refrigerator for 30 days without loss, but beyond that loss was rapid. The frequency with which the stock solution is opened is a major factor in its stability. It is more reliable to prepare solutions of the gases daily. One can prepare stock solutions by transferring the gas from lecture bottle or sampling bag to the alcoholic solution by means of a 5 ml gas tight syringe. Place the syringe needle 1-3 mm above the liquid surface and depress the plunger. Stopper and reweigh. This can be repeated until a desired concentration is reached.

It should be noted that vinyl chloride is no longer available from chemical supply houses, except as a diluted gas standard (1000 ppm). This has made preparation of our own standards impossible.

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COLLECTION AND STORAGE OF SAMPLES

Samples should be collected in 25-100 ml screw capped vials, filled completely and sealed with a Teflon lined silicon rubber septum. A very convenient size is a 40 ml vial (such is available from several suppliers), but a larger vial might be desired depending on the number of analyses necessary.

Samples should be analyzed as soon as possible after collection. However, if properly preserved, samples can be stored up to seven days without substantial loss of volatile organics. Prior to sampling, add one ml 1M phosphate buffer, pH 7.0, containing 5.6 mg/ml sodium sulfite (to reduce 10 ppm residual chlorine). After sampling, the vial should be sealed with no air bubbles and stored at 2-4° C.

ANALYSIS

The purge and trap method using Coulson or FID detectors and the solvent extraction/electron capture method are recommended as acceptable methods for the analysis of volatile organic compounds. Acrolein, acrylonitrile, benzene, toluene, and ethylbenzene are analyzed most successfully by FID purge and trap.

Chromatography

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The following gas chromatographic procedure is recommended when using either the solvent extraction or the purge and trap method of analysis. The analytical scheme assumes the potential presence of all 36 compounds and is based on the use of two analytical columns to give complete separation of all compounds, as well as to provide some confirmation of peak identity. To optimize the analytical time the order of analysis should be:

a. Analyze first on a 1.8m x 2mm ID glass column packed with 1% SP-1000 or 60-80 mesh Carbopack B with a halogen specific detector. On this column all compounds are well separated except for ten compounds. Use a temperature program of: start at 50°C, hold 4 min; increase 10°min to 240° hold 5 min. The column flow rate should be 25 ml/min for nitrogen. If no peaks appear at the retention times of the coeluting compounds, then quantitation of any other compounds can be completed using this column alone. In any event, the next step is to calibrate the analysis, either by running external standards, or by means of adding an internal standard.

b. If the sample appears to have some of the compounds which do not separate on the 1% SP-1000 column, then a run on a 4m x 2mm ID, column packed with 20% SP-2100 on 100-120 mesh Supelcoport column will allow one to determine which of the suspected compounds are present. Again, calibration runs are made using either external or internal standards.

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c. A third run, using either column, with a flame ionization detector will be necessary to detect the non-halogenated compounds.

If retention time correlation and quantitation are obtained from the recorder trace, then repeated runs may be necessary to get all peaks on scale. Analysis time and calculation time will require 5-6 hours per sample, including calibration time, if many compounds are present. The use of internal standards would greatly facilitate quantitation of a large number of compounds. Although the use of internal standards was not studied in this project, their use might be advisable where possible.

Purge and Trap

The following parameters are recommended as optimum conditions of the purge and trap method:

a. Purge volume: 5 ml. The volume can easily be varied between 1-20 ml. Increasing the volume is a convenient way of increasing the detection limit. Since purging efficiency varies slightly with purge volume, then each volume used should be calibrated.

b. Purge temperature: 22-30° C:

c. Purge time: 10 min; longer times should be used if purge volumes are increased over 5 ml.

d. Purge flow rate: 40 ml/min:

e. Desorb time: 5 min;

f. Desorb flow: 25 ml/min - same as GLC carrier gas

g. Desorb temperature: 200°C

h. Trap: 2mm x 21cm glass lined stainless steel filled with 14cm of Tenax and 7cm of Carbosieve B (HT) or SKC charcoal.

Additional study is needed on trap materials. In this study, only a limited amount of time was spent on evaluation of trap materials. Although the Tenax/charcoal combination seems adequate, a number of researchers report [3, 4, 5, 6, 7, 8, 9] that other materials may be more suitable for selected compounds.

The problem of system contamination for high levels (ppm for example) of one or two test compounds, or even some non-test compound, is a very serious one. The time required to clear the purge chamber by continuous purging can be several hours. Rinsing the chamber with solvent and drying with heat can speed up the process, but, even this means a loss of one to two hours. A rapid, effective clean-up method is definitely needed when analyzing industrial effluents. Of the samples analyzed, the samples from

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the organic chemicals industry and the auto and other laundry industry presented these problems.

Solvent Extraction/Electron Capture Detection

The recommendation for this procedure assumes that samples will be collected in 40 ml screw capped vials, sealed with a Teflon lined septum. Pierce the septum with two syringe needles. By means of a 5 ml gas tight syringe remove five ml from the vial through the septum. Add to the vial, using a second syringe, two ml of pentane. Remove the syringe and shake the vial vigorously for one minute. Allow the phases to separate and inject 2-5 microliters of the pentane into the gas chromatograph. The detector sensitivity should be set to see 1ppb of the most responsive compounds. Repeated runs could be made, increasing the sensitivity of the detector each time, until the detection limit for each compound has been reached or until the response of compounds in high concentration mask the detection of other compounds. For the monohalogenated compounds and the dichloroethanes, the response is so weak that detection of levels less than 100 ppb is not very likely.

The above procedure allows one to detect about 13 of the halogenated test compounds in the range 0.1 - 5ppb. The sensitivity of the method can be increased by increasing the extraction ratio; however, increases in extraction ratios will be partially offset by a decrease in extraction efficiency. The presence of head space greatly facilitates the extraction of most compounds, and only the most volatile (the gases) show any loss.

Since making dilutions of the pentane layer is not very practical, it is important for the detector to have a large dynamic range. Older electron capture detectors have notoriously narrow linear response ranges. Making multiple extractions at different extraction ratios can, of course, be done, but this greatly extends the analysis time. Therefore, a linear detector is important. In our calibration runs, the Varian ^{63}Ni electron capture detector was used.

Direct Aqueous Injection

It is recommended that waste water be subjected to preliminary analysis for high levels of volatile pollutants by direct injection of sample before analysis by the above methods. This procedure can readily detect 0.1 - 10 ppm levels of the test compounds. If compounds are present at this level, they will present difficulties in analysis by purge and trap or by solvent extraction. By running a preliminary analysis using direct injection, one can be forewarned and plan accordingly. Quantitation of volatile compounds by direct injection of industrial waste water is not recommended for two reasons: First, occasional "ghost peaks," which seem to be due to interaction of water with the column, can interfere. Second, injection of water seems to have an activating effect upon some columns, which can lead to misleading quantitative results, as described previously.

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